PETROLEUM AND NATURAL GAS RESEARCH BUREAU OF MINES, FISCAL YEARS 1954, 1955, AND 1956

BY A. J. KRAEMER

Information Circular 7940

UNITED STATES DEPARTMENT OF THE INTERIOR
Fred A. Seaton, Secretary
BUREAU OF MINES
Marling J. Ankeny, Director

1959

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This publication has been cataloged as follows:

U.S. Bureau of Mines.
Petroleum and natural gas research. 1950-

Washington.
v. illus. 27 cm. (Its Information circular 7616, etc.)
Supersedes the Report of the Petroleum and Natural Gas Branch.
Title varies slightly.

1. Petroleum—U. S. 2. Gas, Natural—U. S. 3. Petroleum research. (Series)

[TN23.U71 no. 7616, etc.] 622.06173

U. S. Dept. of the Int. Library

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PETROLEUM AND NATURAL GAS RESEARCH, BUREAU OF MINES, FISCAL YEARS 1954, 1955, AND 1956[1]

by

A. J. Kraemer[2]

SUMMARY AND INTRODUCTION

This report on research and experimentation by the Federal Bureau of Mines on technologic and scientific problems of the petroleum and natural gas industries presents a résumé of work from July 1, 1953, to June 30, 1956. The preceding report, for the fiscal year ended June 30, 1953,[3] indicated continuation of the Bureau's program of petroleum and natural gas research of worldwide significance, which began in 1910.

The petroleum and natural gas research of the Bureau of Mines is divided into five main categories: (1) Production of petroleum and natural gas, (2) transportation and storage, (3) petroleum chemistry and refining, (4) thermodynamics, and (5) economics.

The scope of the present report does not include work by the Bureau of Mines on oil-shale and shale-oil research and development. Summaries of those activities for 1954 and 1955 have been published as annual reports of the Secretary of the Interior.[4]

The Bureau of Mines oil-shale demonstration plant at Rifle, Colo., was placed in standby condition June 30, 1955, upon the expiration of funds. Since that time oil-shale research has been continued at the Laramie Petroleum Research Center of the Bureau of Mines, Laramie, Wyo., under the Bureau of Mines regular appropriation.

1/ Work on manuscript completed April 17, 1959.

2/ Staff advisor, Division of Petroleum, Bureau of Mines, Washington, D. C.

3/ Cattell, R. A., and others, Petroleum and Natural Gas Research Program, Bureau of Mines, Fiscal Year 1953: Bureau of Mines Inf. Circ. 7717, 1955, 76 pp.

4/ Bureau of Mines, Synthetic Liquid Fuels, Annual Report of the Secretary of the Interior for 1954, Part II, Oil From Oil Shale: Bureau of Mines Rept. of Investigations 5119, 1955, 115 pp.

Bureau of Mines, Synthetic Liquid Fuels, Annual Report of the Secretary of the Interior for 1955, Part II, Oil From Oil Shale: Bureau of Mines Rept. of Investigations 5237, 1956, 80 pp.

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In this report the work is described mainly in the form of abstracts of publications that have been issued by the Bureau of Mines or in the scientific, technical, and trade press. The total number of publications is large, and some of the same information has been presented in several forms. If a report is out of print in one form of publication, the information may be available in whole or in part from another source. These alternative forms of publication are indicated in the references.

A paper presented before the Secondary Recovery and Pressure Maintenance Committee Meeting of the Interstate Oil Compact Commission, Chicago, Ill., December 2, 1954, described Bureau research on petroleum. An excerpted version of the paper[5/] deals mainly with the drilling and production portions of Bureau research. The article points out that more general recognition of the precepts of true conservation throughout the Nation is a mutual objective of the Bureau of Mines and the Interstate Oil Compact Commission. They are working together to increase America's petroleum supplies by applying better extraction methods. Wise use of the petroleum reserves of the country by converting them into "tailor-made" products to meet an ever widening and exacting consumer demand is a companion need.

Attention is directed to Bureau of Mines research on use of tracers in waterflooding, selective plugging of sands, use of explosives in shooting wells, the nature and effects of surface forces in petroleum production, water in oil and gas wells, type and amount of clays in oil-bearing rocks, and engineering field studies.

Bureau research is described more fully in an article[6/] based upon material supplied by members of the staff of the Bureau of Mines engaged in petroleum research at San Francisco, Calif.; Laramie, Wyo.; Bartlesville, Okla.; Morgantown, W. Va.; Dallas and Wichita Falls, Tex.; and Washington, D. C.

The purpose of the production-research program, as described in the article, is to develop technical data that will promote efficient use of the potential energy associated with underground deposits of petroleum and natural gas and to stimulate flow of these substances to the surface by artificial means when the potential energy of the reservoir system has been partly or totally depleted.

The objective of the program is to improve the two general methods of recovery--primary or flush production and secondary or stimulated production. Such improvements can be achieved through changes in the three major processes of recovery: (1) Gas drive (utilizing the energy from expanding gas), (2) oil-water drive (utilizing natural water pressure), and (3) induced drive (injection of gas, water, or air). Recovery processes are changed as a result of scientific facts developed from study of the variables in the production process, such as reservoir fluid energy, physical and chemical properties of

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5/ Cattell, R. A., Petroleum Research of the Bureau of Mines: Prod. Monthly, vol. 19, No. 5, March 1955, pp. 22-27.

6/ The Mines Magazine, Bureau of Mines Research Related to Petroleum: Vol. 45, No. 10, October 1955, pp. 65-70.

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the reservoir fluid and rock, well spacing, and use of surface and subsurface equipment in producing the fluid.

Bureau research on transportation and storage is conducted to obtain information leading to more efficient transportation of petroleum, natural gas, and their products and to prevent waste of these resources in both surface and underground storage. Safe practice in underground gas-storage projects also is an objective of Bureau research, because of the possible hazard of vertical or horizontal migration of natural gas from storage reservoirs.

There has been a tremendous increase in pipeline transportation of petroleum, natural gas, and their products from the main sources of supply in the Midcontinent and Gulf Coast areas to markets on the west coast, the Northern United States, and the east coast. As a result, there is increasing need for basic information on fluid flow, especially through large-diameter pipelines, to prevent waste of energy and materials. For a number of years the American Gas Association has contributed funds to the Bureau of Mines for basic research on the flow of gas through pipelines at high pressures and at high flow rates, as well as for other research on natural gas problems.

The work on petroleum chemistry and refining was instituted to provide basic information about the properties and composition of crude petroleum, its components and products, and to establish relationships of properties and composition to utilization of the raw material and its products. Such fundamental information helps to develop improved and new products and superior processes and promotes more efficient production and utilization of petroleum.

Nationwide surveys in cooperation with industry are continually in progress to determine the quality and characteristics of petroleum products. These surveys serve as guides for the refining industry and the consuming public and are a comprehensive source of information to the Government.

Research on the nature and reactions of sulfur and nitrogen compounds in petroleum, financed in part by industry through the American Petroleum Institute, provides information useful in developing processes for efficient utilization of crude oils containing troublesome amounts of sulfur and nitrogen. Other projects, financed in part by industry and other Government agencies, provide information concerning the composition and availability of aviation and diesel fuels, their stability and compatibility characteristics; and effects of composition, chemical additives, and engine operating conditions upon combustion of these fuels.

Research in thermodynamics is conducted to obtain accurate data for hydrocarbons and related substances found in petroleum and for chemical compounds that may be manufactured from petroleum components. Thermodynamic properties are used to predict optimum conditions of temperature and pressure for chemical reactions and for plant processes. Such studies guide research work and assure proper plant design for efficient utilization of materials and manpower. The program is supported financially through cooperative agreements with the American Petroleum Institute and by a working fund from the Air Research Development Command.

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The Branch of Petroleum Economics compiles petroleum and natural gas statistics and issues regular weekly, monthly, and annual reports covering various branches of the industry. These statistics are based upon data submitted by the industry on questionnaires mailed from the Washington and San Francisco offices. The reports cover production, transportation, storage, and refining of crude oil and the manufacture, transportation, storage, and sales of refined products. The same type of coverage is obtained for the natural gas and natural gas liquids industries.

These published reports, about 150 a year, picture the current supply-demand position of the industry and also give a consistent set of historical statistics for measuring trends.

ACKNOWLEDGMENTS

This account of the published results of Bureau of Mines work on petroleum and natural gas from July 1, 1953, to June 30, 1956, was prepared mainly from publications written by Bureau staff members. The author is grateful for assistance given in compiling this report by staff members of the Washington and regional offices, field offices, and Petroleum Research Centers and Laboratories.

PETROLEUM AND NATURAL GAS DEVELOPMENT AND PRODUCTION

The Bureau of Mines has been conducting research on the production of petroleum and natural gas since it was established in 1910. This research has included studies of well-drilling, production, and transportation and storage of petroleum and natural gas.

Secondary-Recovery Research

A series of four articles on secondary-recovery research by the Bureau of Mines[7/] describes its work in this field at its Morgantown Petroleum Research Laboratory, Morgantown, W. Va.; Bartlesville Petroleum Research Center, Bartlesville, Okla.; Laramie Petroleum Research Center, Laramie, Wy.; San Francisco Petroleum Research Laboratory, San Francisco, Calif.; and petroleum field offices at Dallas and Wichita Falls, Tex.

7/ (a) Wertman, Wm. T., Tignor, E. M., and Taylor, Sam S., Secondary Recovery Research, U.S. Bureau of Mines: Prod. Monthly, vol. 20, No. 5, March 1956, pp. 20-25.
(b) Fowler, H. C., U.S. Bureau of Mines Secondary Recovery Research, Mid-Continent and Gulf Coast Regions: Prod. Monthly, vol. 20, No. 6, April 1956, pp. 24-29.
(c) Baptist, Oren C., U.S. Bureau of Mines Secondary Recovery Research, Rocky Mountain Region: Prod. Monthly, vol. 20, No. 7, May 1956, pp. 31-35.
(d) Shea, G. B., U.S. Bureau of Mines Secondary Recovery Research, Pacific Coast Area: Prod. Monthly, vol. 20, No. 8, June 1956, pp. 46-50.

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Eastern Area

The Bureau of Mines Morgantown Petroleum Research Laboratory, adjacent to the campus of the University of West Virginia, serves an area comprising 12 States in which petroleum is produced: Alabama, Florida, Illinois, Indiana, Kentucky, Michigan, New York, Ohio, Pennsylvania, Tennessee, Virginia, and West Virginia.8/ According to the American Petroleum Institute (API), the proved reserve of this area is 1,077,130,000 barrels of oil; moreover, it is estimated that known petroleum reservoirs in these States contained 15 billion barrels of oil at the end of 1954.

At the time the report was written the Bureau of Mines petroleum-research program at the Morgantown Petroleum Research Laboratory consisted of seven subjects: (1) Engineering studies of selected oilfields, (2) special and routine analyses of reservoir rocks, (3) pore studies of petroleum-reservoir sandstones, (4) electric logging of formations in wells, (5) flowing versus pumping oil-producing wells on waterflood projects, (6) shooting boreholes with explosives to increase conductivity of sandstones, and (7) underground storage of natural gas.

Midcontinent and Gulf Coast Areas

The Bartlesville Petroleum Research Center at Bartlesville, Okla., and closely associated field offices at Dallas and Wichita Falls, Tex., contribute an integral and important part to the petroleum-research program of the Bureau of Mines. The article by H. C. Fowler9/ tells only of secondary-recovery research at the Bartlesville Research Center and the two field offices in Texas. The discussion is divided into two main sections: (1) Characteristics of reservoirs, and (2) reservoir performance and production techniques. Results of the studies described have emphasized the great advantage that accrues to industry and to Government through the cooperative use of technical and scientific personnel in long-view research on fundamentals; at the same time the needs of the hour have been recognized, and work on problems of immediate importance has not been neglected.

Rocky Mountain Region

The art of stimulating petroleum production by adding energy to the formations has not been practiced widely in the Rocky Mountain region.10/ Perhaps this lag in applying secondary-recovery methods that have proved so successful in the Eastern and Midcontinent regions has been due partly to the distance from markets, the large number of operators involved in many of the unit operations, and, until recent years, the lack of adequate pipeline transportation to move the available oil to markets outside the area. Almost continuously, from the time of development of the Salt Creek field in 1917 until World War II, the productive capacity of the developed fields in the area was greater than the local demand. The first major pipeline connecting the area

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8/ Work cited in footnote 7, item (a), p. 4.
9/ Work cited in footnote 7, item (b), p. 4.
10/ Work cited in footnote 7, item (c), p. 4.

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with midwestern markets was completed in 1924, but only in recent years has pipeline capacity been expanded to accommodate the total production from the area.

In 1948 the Congress recognized the need for Federal research on the multitude of problems connected with secondary recovery and appropriated funds to the Bureau of Mines to aid in making additional supplies available in peace as well as in war. Research on problems of special interest to operators in the Rocky Mountain region was begun under this project at Laramie, Wyo., in 1949 and had been continued on a modest scale to the time the article was written.

The project was originally planned to include both field tests and laboratory research; however, funds have been available only for laboratory work. The laboratory at Laramie, adjacent to the campus of the University of Wyoming, is well-equipped for research on the physical properties and behavior of reservoir rocks.

Figure 1 shows the equipment used at the Laramie Petroleum Research Center in testing the capillary behavior of oil-reservoir sands. Mercury-injection and capillary-pressure equipment is in the foreground, and water-and-gas-permeability apparatus is in the background.

The different studies under the program deal with: (1) Physical properties of reservoir rocks; (2) recovery of oil from producing formations by waterflood and gas drive; (3) clay content of reservoir sands; (4) effect of clay on permeability of wells that have been killed with water; (5) capillary properties and behavior of reservoir sands and correlations of these characteristics with other physical properties; and (6) development of improved methods for studying clay minerals in reservoir rocks and better tests for determining the swelling capacity of each of the clays.

Pacific Coast Area

Following World War II the steadily increasing demand for petroleum products and decreased ratio of discovery of new oilfields in California intensified exploration work in wildcat areas throughout the State.[11/] The industry's thinking also was diverted in another direction--application of secondary-recovery methods to obtain additional oil from many depleted and partly depleted fields. The first waterflood in California was undertaken in 1946; and, as demand for crude oil began to outstrip supply, the number of projects for increasing ultimate recoveries of oil by water injection increased in number and extent. The thick, complex, nonuniform oil sands in California, with extreme variations in permeability, yielding viscous crude oils of low API gravity, and swelling of the argillaceous content of some reservoir sands by water offer the main difficulties to waterflooding.

Because of the importance of secondary recovery to the future of the oil industry in California, the Bureau of Mines Petroleum Research Laboratory at

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11/ Work cited in footnote 7, item (d), p. 4.

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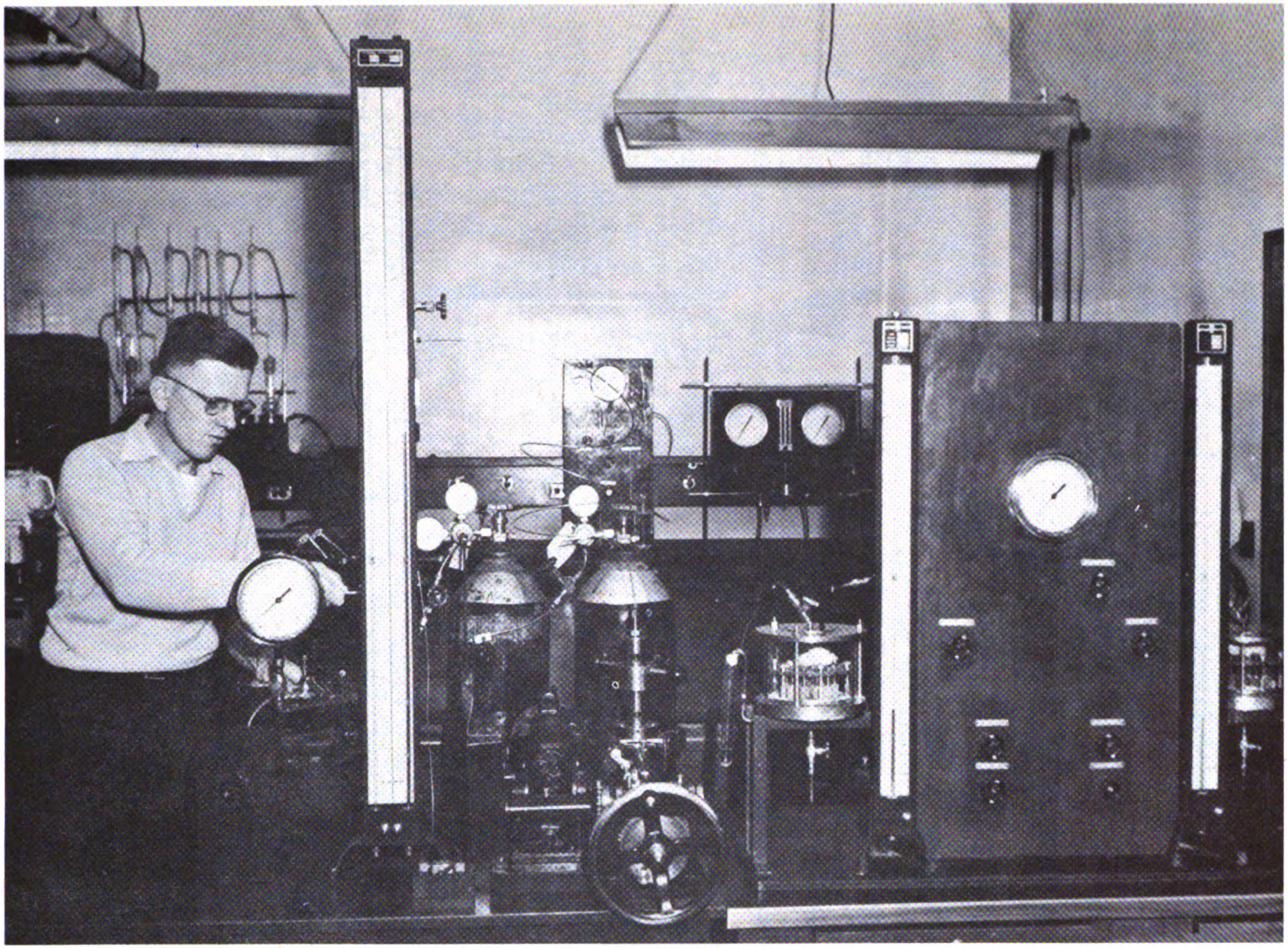

FIGURE 1. - Testing the Physical Properties and Capillary Behavior of Oil Reservoir Sands. Mercury-Injection and Capillary-Pressure Equipment Is in the Foreground and Water- and Gas-Permeability Apparatus Is in the Background.

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San Francisco initiated a secondary-recovery research program in 1949 to develop basic laboratory and field data on the problems associated with gas and water injection. The major items of the research program were: (1) Measurement of relative permeability to gas, oil and water in gas-oil and in water-oil systems, (2) identification of the types of clay minerals in California oil-reservoir rocks and determination of their deleterious effect on productivity, (3) determination of the electrical resistivity of the waters produced from the important oil-producing formations in California, (4) measurement of surface areas of clays and sedimentary rocks, (5) study of well-completion practice, and (6) appraisal of oil-recovery mechanisms.

Field-Engineering Studies

In this section studies by the Bureau of Mines of conditions and operating practices in petroleum and natural gas fields are described, and contents of published reports are summarized.

Kansas

Burkett and York-Demalorie C

Injection of water into one or more wells in a field is one of the methods of induced drive used to increase the recovery of petroleum. The Burkett Unit and the York-Demalorie C floods are typical of many successful waterflooding projects in Greenwood County, Kans.[12/] The York-Demalorie C flood in the Seeley-Wick pool was the first legal waterflooding project in Kansas. It was begun in May 1935. The Burkett unit, composed of approximately 900 acres, was unitized January 1, 1939, and a gas-injection program was begun that year. Water injection was begun about August 1942, and the total recovery of oil since then exceeds 5.1 million barrels. Approximately 37.5 million barrels of water was used, or approximately 7 barrels of water for each barrel of oil recovered during the flood.

The York-Demalorie C lease (180 acres) is part of a waterflooding project begun in 1935 in the Seeley-Wick field. Approximately 626,000 barrels of oil was recovered from the lease by primary methods between 1925 and 1935. About 9.6 million barrels of water was injected in the 20-year period to produce 622,000 barrels of oil.

Butler and Greenwood Counties

Another publication on waterflooding in Kansas[13/] presents a discussion of four projects: (1) The Morrison Producing Co. Fox-Bush project in Butler County, Kans., (2) the Cities Service Oil Co. El Dorado Shallow-Sand project in the El Dorado field, (3) the Tidewater Associated Oil Co. Blankenship

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12/ Taliaferro, D. B., and Eakin, J. L., Burkett Unit and York Demalorie C (Kans.): Oil and Gas Compact Bull., vol. 14, No. 1, June 1955, pp. 110-114.

13/ Powell, J. P., Water Flooding of Oil Sands in Butler and Greenwood Counties, Kans.: Bureau of Mines Inf. Circ. 7750, 1956, 42 pp.

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project on the Blankenship-Sallyards pool, Butler County, Kans., and (4) the Ohio Oil Co. Bryden-Ladd unit project in Greenwood County, Kans. Figure 2 shows a water-treating plant of the Tidewater Associated Oil Co. When the report was written the projects had been in operation 6 to 12 years and had recovered about 6.6 million barrels of additional oil from injection of 84.7 million barrels of water. Discussion of the individual projects includes information on the early history, the source and treatment of water used for flooding, production-decline curves, typical electric logs and core analyses, water analyses, sketches of the water-conditioning systems, and results of waterflooding.

The report has been published in portions in two petroleum journals.[14/]

Southeast Kansas

A report[15/] on waterflooding in five counties in southeast Kansas was prepared under a cooperative agreement with the Kansas State Board of Health and with the cooperation of officials and employees of the oil companies and many individual owners who operated the waterflooding projects and furnished data regarding their respective projects.

Most waterflooding projects in the area had been developed to flood the Bartlesville sand, although some are in the Burgess or the Squirrel sand; a pilot plant had been started to test the Dennis sand.

Development, production practices, and source and treatment of water are outlined briefly, and individual projects are discussed in detail. It was estimated that, to July 1, 1955, the 77 projects resulted in the recovery of 12.3 million barrels of oil that would not have been produced by methods used

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14/ Powell, J. P., Producers' Monthly Articles as follows: Water Flooding of Oil Sands, Fox-Bush Project: Vol. 20, No. 8, June 1956, pp. 22, 24, 25; Waterflooding of Oil Sands, El Dorado Shallow Sand Project: Vol. 20, No. 9, July 1956, pp. 33, 34; Blankenship Water-Flood Project: Vol. 20, No. 11, September 1956, pp. 45-47; Bryden-Ladd Water-Flood Project: Vol. 20, No. 12, October 1956, pp. 41-43; Baird Oil Co. Water Flood in Washington County, Okla.: Vol. 21, No. 8, June 1957, pp. 18-21; Bonaventure Oil Corp. Wayside Water Flood Project, Washington County, Okla.: Vol. 21, No. 9, July 1957, pp. 30-31; Signal Oil Co.'s Flood 3 Project: Vol. 21, No. 10, August 1957, pp. 28-30; Fred P. Schonwald Morrison Project: Vol. 21, No. 12, October 1957, pp. 34-35.
Oil and Gas Journal as follows: Water Flooding Pays Off for Two Companies: Vol. 54, No. 69, Aug. 27, 1956, pp. 94-96; Chesney Plant Typical of El Dorado Units: Vol. 54, No. 77, Oct. 22, 1956, pp. 116-118; Tidewater's Blankenship Water Treating Plant: Vol. 55, No. 1, Jan. 7, 1957, pp. 126-127; and Ohio Oil's Bryden-Ladd Water-Flood Treating Plant: Vol. 55, No. 2, Jan. 14, 1957, p. 118.

15/ Powell, J. P., Survey of Water-Flooding Projects in Allen, Bourbon, Crawford, Labette, and Neosho Counties, Kans.: Bureau of Mines Rept. of Investigations 5317, 1957, 172 pp.

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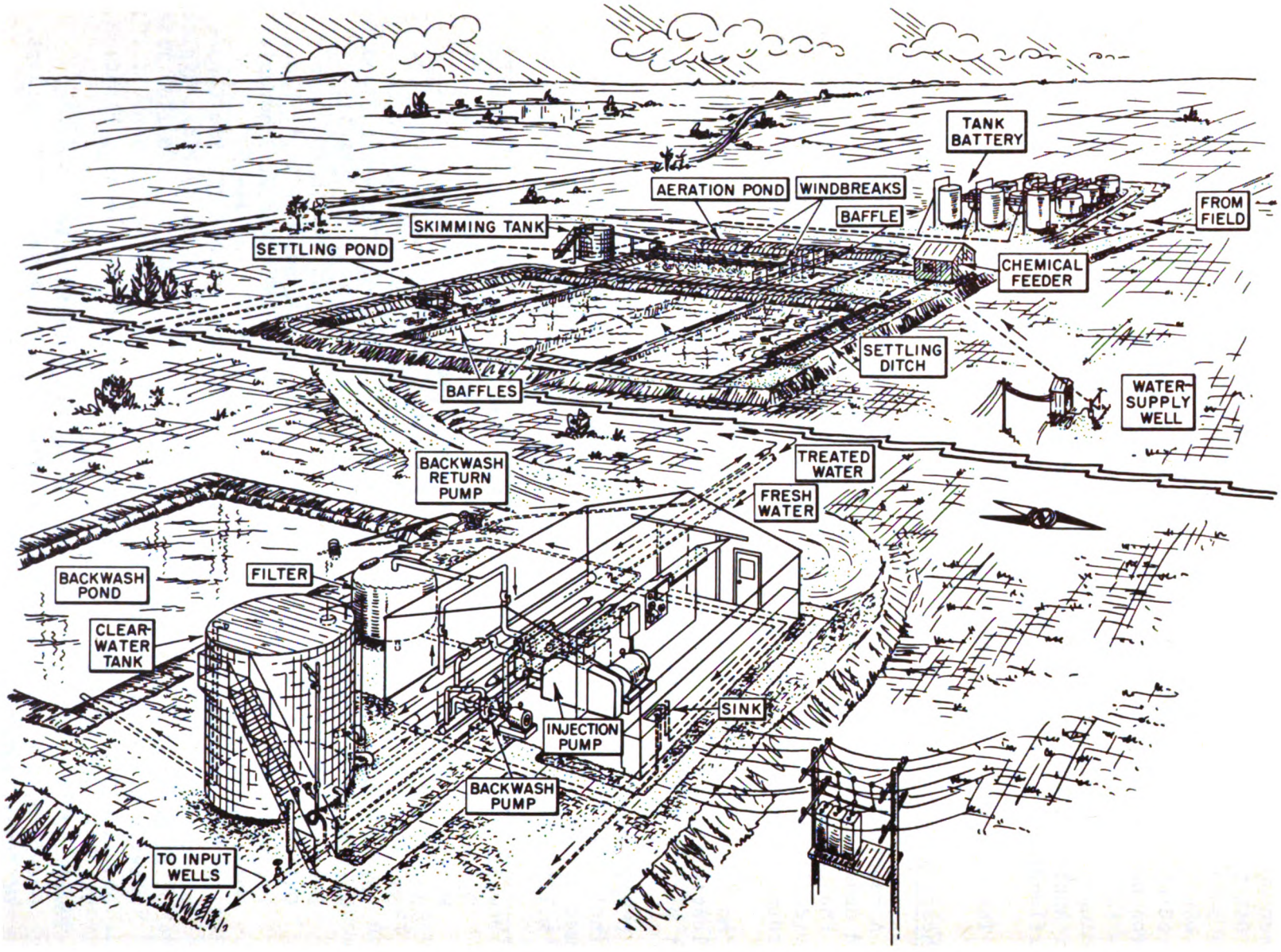

FIGURE 2. - Water-Treating Plant of Tide Water Associated Oil Co. Hull Lease, Blankenship Project, Greenwood County, Kans.

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previously. The projects are expected ultimately to cover 10,700 acres, of which only 5,400 acres had been subjected to flooding when the report was written.

Oklahoma

Flat Rock Oilfield

A report of an engineering study of the Flat Rock oilfield, Osage County, Okla.,[16] describes the geology, reviews the production history, presents a complete reservoir analysis, and estimates remaining oil reserves. The field was discovered in November 1904 and was one of the first of many Bartlesville-sand fields developed in eastern Osage County during the early part of the 20th century. Although substantial oil reserves remain in the pressure-depleted sands in some parts of the field, their economic recovery by waterflooding will require careful consideration of the many factors involved.

Burbank Oilfield

A report[17] was prepared and published in mimeographed form by the Bureau of Mines Petroleum Research Center, Bartlesville, Okla., as a service to oil producers interested in waterflooding in Osage County, Okla., particularly the projects in the Burbank fields. The report was designed to supplement the tour of the Burbank projects by the Kansas-Oklahoma Water Flooding Operators, the Northeast Oklahoma Oil Producers Association, and the Kansas Section of the American Institute of Mining and Metallurgical Engineers on May 12, 1954. The three major waterfloods in western Osage County are described, and a map of the area shows the location of five waterflood units and the main distribution lines for the system supplying water for the floods.

Nowata County

The fifth in a series of reports[18] covering waterflooding operations in Nowata County, Okla., presents a discussion of four full-scale waterflooding projects in the Delaware-Childers field and one pilot project in the Curl Creek field. All five plants had been in operation for only a few months when the report was prepared. Although substantial increases in the rates of oil production had been obtained by the injection of water, the projects are of particular interest because of the novel methods of operation and new equipment employed.

16/ Riggs, C. H., Wey, J. E., and Maude, J. V., Petroleum-Engineering Study of Flat Rock Oilfield, Osage County, Okla.: Bureau of Mines Rept. of Investigations 5018, 1954, 42 pp.

17/ Riggs, C. H., Water Flooding in the Burbank Oil Field, Osage County, Okla.: Bureau of Mines Pamphlet, mim., 1954, 19 pp. Also, Prod. Monthly, vol. 18, No. 8, June 1954, pp. 33-38; Oil Gas Jour., vol. 53, No. 26, Nov. 1, 1954, pp. 88-93; World Oil, vol. 139, December 1954, pp. 182, 184-186, 188.

18/ Eakin, J. L., Recent Developments in Waterflooding in Nowata County, Okla., Oilfield, 1954-55: Bureau of Mines Rept. of Investigations 5134, 1955, 49 pp.

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The discussion of the individual projects includes information on the source and treatment of the water used for flooding, early history and lease development maps, production-decline curves, typical core analyses, water analyses, and pictorial drawings of the water-treating plants. The projects were too new to permit an analysis of the result of the operation.

Texas

Scurry Reef Field

The effect of changes in field separator pressures and temperatures on resulting petroleum production data of reef wells in the Scurry County, Tex., field was studied by Bureau of Mines engineers.19/ To determine these effects subsurface oil samples and subsurface pressure and temperature data were obtained, and a series of production gas-oil ratio tests were made on a reef well centrally located in the Kelly-Snyder area of the field. The effect of varying separator temperatures was determined from field gas-oil-ratio tests, and the effect of varying separator pressures was determined from flash gas-liberation experiments conducted in the laboratory on portions of the subsurface oil samples.

Results of these tests showed that normal differences, either in separator pressure or temperature, as found from one tank battery to another in the Scurry Reef field, influenced materially the measured production gas-oil ratios, stock-tank oil gravities, separator-gas gravities, and relative oil volumes (formation volume factors).

Anderson and coworkers20/ describe the casing programs and well-completion methods used by operators in developing the Kelley-Snyder and Diamond M fields in the Scurry Reef reservoir, and discuss the analyses of cores and other data obtained by Bureau engineers. The volume of stock-tank oil initially in place in the Scurry Reef reservoir was estimated to be 3,668,000,000 barrels, of which 152,940,000 barrels (4.17 percent) had been produced to January 1, 1954. This production was accompanied by a decline in reservoir pressure from an initial of 3,137 p.s.i.a. (pounds per square inch absolute) to 1,587--about 300 p.s.i. below the saturation pressure of the reservoir oil. The majority of the operators entered into unitization agreements whereby greatly increased ultimate oil production is anticipated through the application pressure maintenance by water and gas injection.

19/ Cook, Alton B., Spencer, G. B., Bobrowski, F. P., and Chin, Tim, Scurry Reef Field, Scurry County, Tex.; Changes in Gas-Oil Ratios With Variations in Separator Pressures and Temperatures: Petrol. Eng., vol. 26, No. 2, March 1954, pp. B-77, B-78, B-80, B-82.

20/ Anderson, K. F., Meadows, Paul, Hawkins, Murphy E., and Elliott, William C., Jr., Petroleum Engineering Study of Scurry Reef Reservoir, Scurry County, Tex.: Petrol. Eng., vol. 26, No. 9, August 1954, pp. B-62, B-65, B-66, B-68--B-70, B-72, B-74.

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Variations in Physical Properties of Reservoir Oil

Bureau of Mines engineers developed a method to determine the physical properties of the oil in all parts of a reservoir.[21] The method involves correlation of data from: (1) A survey of the gravity of the produced crude oil, (2) measurements of gas-oil ratios in key wells selected to give representative data for the entire reservoir, and (3) laboratory analyses of reservoir oil samples.

Analyses of subsurface oil samples, with data on reservoir pressures and temperatures, showed that the Scurry Reef reservoir oil originally was undersaturated with gas.

Data from laboratory tests on subsurface-oil samples obtained from seven wells indicate that the physical properties of the oil throughout the reef reservoir have only minor differences--the differences being related directly to the saturation pressure of the reservoir oil.

Big Lake Field

The report of an engineering study of the Ellenburger reservoir in the Big Lake field[22] points out that the increasing number of oil-productive reservoirs in the Ellenburger formation emphasizes the need for information pertaining to the yields of hydrocarbons that may be obtained. The Ellenburger reservoir in the Big Lake field was selected for study because it was one of the few near-depleted reservoirs in the area. Experience gained in operating and developing this reservoir has been, and should continue to be, a helpful guide to operators in predicting recovery and in establishing methods of development and operation in similar reservoirs.

The Ellenburger reservoir in the Big Lake field was discovered December 1, 1928, when high-pressure gas was found at 8,525 feet. It was the first reservoir to produce from the Ellenburger formation in West Texas, and at that time was the deepest reservoir in the world producing oil and gas. Calculations presented in the report indicated that the Ellenburger reservoir was 95 percent depleted when the study was made and that the ultimate recovery of hydrocarbon liquid from the oil reservoir and gas cap combined would be 40 barrels per gross acre-foot of reservoir rock.

21/ Cook, Alton B., Spencer, G. B., Bobrowski, F. P., and Chin, Tim, A New Method of Determining Variations in Physical Properties of Oil in a Reservoir, with Application to the Scurry Reef Field, Scurry County, Tex.: Bureau of Mines Rept. of Investigations 5106, 1955, 47 pp.

22/ Anderson, K. F., Elliott, W. C., Jr., and Moore, J. L., Petroleum Engineering Study of the Ellenburger Reservoir, Big Lake Field, Reagan County, Tex.: Bureau of Mines Rept. of Investigations 5048, 1954, 28 pp.

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KMA Field

A study of the results from 10 pilot waterfloods in the KMA field[23/] in Texas proved that oil can be moved through the KMA reservoir by injection of water. To January 1, 1954, 174,297 barrels of net waterflood oil had been recovered from 956 acres that had been or were being waterflooded. The report includes a map showing locations of the waterflood projects and a table of salient data on waterfloods in the KMA field.

Waterflooding was begun in June 1950 and has been expanded continuously. Initially all the wells took the water under a vacuum at the wellhead, but gradually pressure was needed for water injection. The pressures increased gradually, and by January 1, 1954, injection pressures ranged from 150 to 350 p.s.i. at the wellhead. Pertinent graphic and tabulated data on the progress of the project are given.

Although waterflooding in the KMA field was still in its infancy when the report was written, the active and abandoned waterfloods, both successful and unsuccessful, had proved definitely that oil can be moved through the reservoir by the injection of water. Prolonged operation of floods in a pilot stage, regardless of the results obtained, may have harmful effects on the volume of oil that can be recovered by an expanded program. If the results obtained within a reasonable time are unfavorable, either the trouble should be ascertained and remedied or the injection of water discontinued temporarily until a decision can be reached regarding the future status of the project. If the results obtained are favorable, the flood should be expanded into full-scale operation or the injection of water should be discontinued until the expanded program can be placed in operation.

The KMA report was prepared at the request of the North Texas Section of the American Institute of Mining and Metallurgical Engineers and the Production Committee of the North Texas Oil and Gas Association. The part of the report prepared by the Bureau of Mines was done under a cooperative agreement with the North Texas Oil and Gas Association.

Arkansas

Stephens Field

A report[24/] describes the production history and the geology of the Buckrange (Upper Cretaceous sandstone) reservoir and presents pertinent

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23/ Dobyns, R. P., Burchett, C. T., Jr., McBride, D. S., and Darnes, R. R., Waterflooding Activities in the KMA Field: Petrol. Eng., vol. 27, No. 4, April 1955, pp. B-90--B-96; vol. 27, No. 5, May 1955, pp. B-64, B-67, B-68, B-70--B-73; vol. 27, No. 6, June 1955, pp. B-87, B-88, B-90--B-94; vol. 27, No. 7, July 1955, pp. B-64, B-66, B-68, B-70, B-74; vol. 27, No. 9, August 1955, pp. B-99--B102, B-104.

24/ Meadows, Paul, and Hawkins, Murphy E., Secondary-Recovery Potentialities of the Buckrange Reservoir, Stephens Oilfield, Columbia Nevada, and Ouachita Counties, Ark.: Bureau of Mines Rept. of Investigations 5211, 1956, 40 pp.

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reservoir data. The reservoir was approaching the economic limit of production under operating conditions when the study was made. Over 100 million barrels of oil remaining in the reservoir was not recoverable by primary producing methods. The study was made by the Bureau of Mines in cooperation with the Arkansas Oil and Gas Commission to aid operators in evaluating secondary-recovery possibilities in the reservoir and in planning secondary-recovery programs if it is decided to undertake them.

Wyoming

Rock River Oilfield

A narrative account of the history and development of the Rock River oilfield, known also as the Rock Creek oilfield, was contributed to the Eighth Annual Field Conference of the Wyoming Geological Association.25/ The field in Carbon County, Wyo., was discovered in May 1918 with initial production of 50 barrels of oil daily from the Muddy sand at 2,581 to 2,609 feet. Oil has been discovered also in the Dakota, Wall Creek, and Sundance sands. A total of 117 wells has been drilled in the field. The article contains a structure contour map of the field, a chart of yearly oil production from 1920 to 1952, and Bureau of Mines routine analyses of a sample of crude oil from the Dakota sandstone and one from the Sundance sandstone. Total production of the field through 1952 was 29,355,011 barrels of oil and 18.2 billion cubic feet of gas.

Williston Basin

A special report26/ deals with petroleum in the Williston Basin from the viewpoints of the geography and climate of the area, marketing facilities, geology and geophysical activity, leasing, drilling, and characteristics of formation waters and oil found in the area. A bibliography of 53 references is included.

An appendix gives complete Bureau of Mines routine analyses of 22 samples of petroleum from fields in North Dakota and Montana and describes the characteristics of the oils.

Some factors that should be considered when determining the feasibility of waterflooding the Buckrange reservoir are mentioned.

25/ Espach, Ralph H., and Biggs, Paul, The Rock River Oilfield: Wyoming Geol. Assoc. Guidebook, 8th Ann. Field Conf., 1953, pp. 161-164.

26/ Lindsey, K. B., Petroleum in the Williston Basin, including Parts of Montana, North and South Dakota, and Canada, as of July 1953: Bureau of Mines Rept. of Investigations 5055, 1955, 70 pp.

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Study of Reservoir-Oil Samples

Lance Creek Oilfield, Wyoming

A report on a reservoir in the Lance Creek oilfield[27/] is concerned primarily with presenting laboratory analysis data for 11 subsurface oil samples obtained from six wells in the field and discussing interpretations of the results. The original subsurface sampling of oil in the West Basal Sundance reservoir, Lance Creek oilfield, was done by the Bureau of Mines in June 1937, about 2 years after discovery of the reservoir. The field was sampled to obtain data concerning saturation pressure, solution gas-oil ratio, and shrinkage of the reservoir oil in a reservoir from which little oil had been produced. At this early date only meager data of this type were available for petroleum reservoirs. Figure 3 shows the apparatus used at the Laramie Petroleum Research Center for making a differential gas-liberation analysis of a subsurface sample of reservoir oil.

Unitization of the West Basal Sundance reservoir became effective January 1, 1938. The pressure-maintenance program of injecting gasoline-plant residue gas into the reservoir was started in February 1938. Additional subsurface oil samples were obtained from selected wells in 1941, 1947, and 1948, primarily in an attempt to observe what effect the injected plant-residue gas might have on reservoir oil characteristics over a period of time.

Calculations of the theoretical recovery that might have been obtained with a solution-gas drive have been compared with estimated ultimate recovery under the pressure-maintenance program and indicate that a substantial increase in oil, 9 to 10-1/2 million barrels, will be obtained as a result of the program. This represents a 50- to 64-percent increase in recovery, excluding recovery of liquefied-petroleum gas (P-gas).

Productivity of Wells and Reservoir Performance

Undersaturation and Supersaturation

The productivity of wells and the performance of reservoirs have been studied by Bureau of Mines petroleum engineers. A paper dealing with undersaturation and supersaturation[28/] is concerned with the magnitude of the amount of supersaturation that occurs in an underground reservoir during the flow of oil and gas to wells, and the amount of undersaturation that occurs during repressuring of an oil reservoir where some effective permeability to gas exists. The results showed that gas diffuses rapidly enough so that, for

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27/ Cupps, C. Q., Espach, R. H., and Fry, Joseph, The Effect of Injected Gas Upon the Characteristics of Oil in the West Basal Sundance Reservoir, Lance Creek Oilfield, Niobrara County, Wyo.: Bureau of Mines Rept. of Investigations 5069, 1954, 84 pp., 21 figs.

28/ Higgins, R. V., Study of Undersaturation During Repressuring and Supersaturation During Flow of Oil to Wells: Trans. AIME, vol. 201, 1954, pp. 230-236; Jour. Petrol. Technol., vol. 6, No. 9, September 1954, pp. 127-133.

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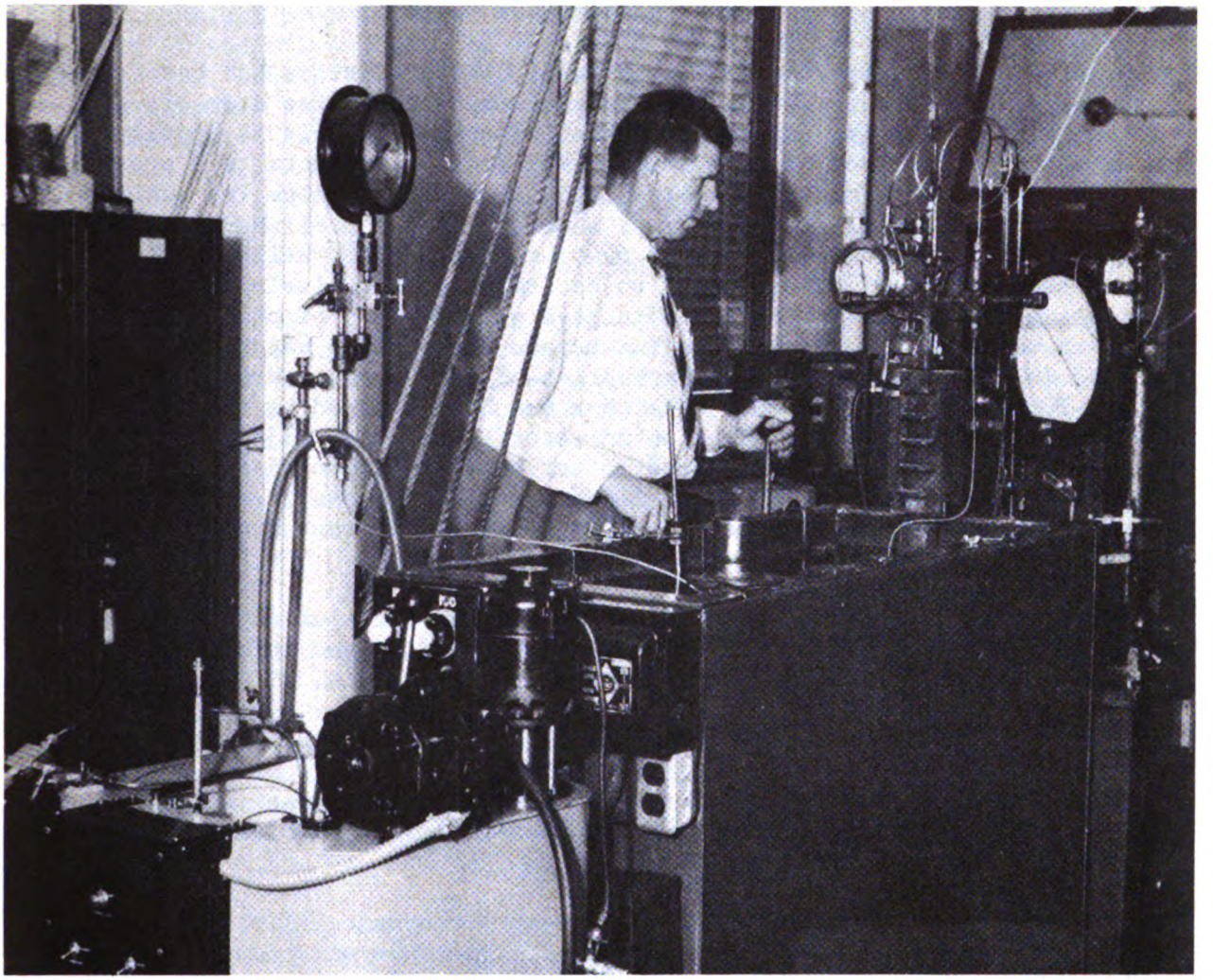

FIGURE 3. - Making a Differential Gas Liberation Analysis of a Subsurface Sample of Reservoir Oil.

all practical purposes, no supersaturation exists during the flow of oil to wells or undersaturation during repressuring in reservoir sands having some effective permeability to gas.

The reason diffusion of the gas virtually keeps the oil saturated is the long time required in radial flow for oil to reach the well and the slow rate at which pressure in reservoirs is increased during repressuring.

The report contains results of a study of the factors that influence the degree of nonequilibrium of the phase relations of oil and gas through reservoirs to wells and also during injection of gas into partly depleted sands. Data from an underground reservoir are presented, and the degree of supersaturation during the flow of the oil through the reservoir to the well is approximated. Also, data from another reservoir are used, and the degree of unsaturation during the repressuring operation is calculated.

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Testing Water-Input Wells

Useful knowledge of formation and well characteristics has been derived by analysis of pressure-buildup and pressure-decline curves from oil-production wells. As similar information about water-input wells is equally useful in operating waterflooding and pressure-maintenance projects, the pressure-buildup method of testing oil wells was studied to determine its applicability to testing input wells.29/ The study showed that the published equations that describe the pressure-buildup behavior of oil-production wells may be used, with a few additional assumptions, to determine qualitatively the efficiency of input-well operations and the effective permeability of producing formations to water. The pressure-decline method for testing water-input wells described in this article permits evaluation of the pressure drop in that part of the formation near the well bore that has been damaged by the completion of the well or by subsequent injection of water. Damage by injection water could result from deposition of suspended matter, precipitation of solids as a result of chemical action, or the swelling of clays. Pressure-decline curves have been recorded for 35 water-input wells in 5 different production areas in northeastern Oklahoma and eastern Kansas.

The paper presents a brief review of the pressure-buildup analysis, a discussion of its applicability to water-input wells, and an analysis of several pressure decline curves recorded during field tests.

Solution-Gas-Drive Reservoirs

An outstanding contribution to petroleum technology was made in a report30/ that provided answers to petroleum-reservoir problems that had long been a matter of concern to engineers.

Methods used to appraise the long-range performance of petroleum reservoirs are based upon physical properties of the crude oil and the permeability of the reservoir rock. By means of these methods the performance of a reservoir may be estimated through its entire life. Before these methods were used, the future performance was estimated mainly by extrapolating pressure-decline curves--a method that normally is satisfactory for extrapolating only for a short period into the future.

Selection of the physical properties of the samples to represent those of the oil and rock for the entire reservoir is difficult. The report is concerned with the error in calculated recoveries that may result from these inherent difficulties.

29/ Joers, J. C., and Smith, R. V., Determination of Effective Formation Permeabilities and Operation Efficiencies of Water Input Wells: Petrol. Eng., vol. 26, No. 11, October 1954, pp. B-82--B-96; Prod. Monthly, vol. 18, No. 12, October 1954, pp. 21-28.

30/ Higgins, Ralph V., Calculating Oil Recoveries for Solution-Gas-Drive Reservoirs. Evaluation of Permissible Errors in P.V.T. Data and k_g/k_o Ratios: Bureau of Mines Rept. of Investigations 5226, 1956, 24 pp.

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The physical properties of the crude oil used in the calculations are the viscosity of the oil and gas phases, the gas solubility, and the formation-volume factor. These properties can be measured accurately in the laboratory. Specific examples and details are presented to guide reservoir engineers in approximating the influence of the various factors on recovery.

Well Completion

Pressure-Buildup Evaluation

It is generally recognized that the productivity and ultimate recovery of an oil well may be reduced as a result of reduction in permeability of the sand at the well bore by invasion of filtrates and clay particles from drilling fluids. Because of growing recognition of the importance of completion practices as related to the quantity of oil that may be recovered from wells, the Bureau of Mines studied completion practices in California and the Midcontinent area. Morris[31/] presents an evaluation of the effect of clay-water and oil-base completion fluids on the productivity of 22 Stevens-sand wells in Kern County, Calif.

Results of this study indicate that the danger of creating a reduced permeability annulus about the well bore is minimized where completion practice includes the use of an inert drilling fluid that will not add water to the reservoir formation or react with clay minerals that may be present. The results also show that the length of time the drilling fluid is in contact with the producing formation during completion operations should be reduced to a minimum if maximum productivity is to be obtained.

Oil-Well Shooting

Field and laboratory tests on oil-well shooting are described in a report[32/] on a cooperative project conducted jointly by the Applied Physics Research Laboratory, College Park, Md., and the Morgantown Petroleum Research Laboratory, Morgantown, W. Va.

The 1954 field tests consisted of six experimental shots of explosives in relatively deep holes in a sandstone similar to many oil-bearing sandstones. Water-injection measurements were made before and after each shot to establish the change in conductivity of the fluid caused by the shot. Results of water-injection tests showed the range of conductivity of fluid before and after shooting with two different types of explosives. A series of laboratory tests was conducted concurrently with the field tests to investigate the effect of liquid content on the strength of sandstone. Five recommendations regarding future experiments of this type are given in the report.

31/ Morris, Frank C., A Correlation of Pressure Buildup in Oil Wells With Completion Practice for a Deep California Field: Bureau of Mines Rept. of Investigations 5333, 1957, 27 pp.

32/ Rough, Robert L., Progress Report on Oil-Well-Shooting Research--1954 Tests: Bureau of Mines Rept. of Investigations 5345, 1957, 21 pp.

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Special Field Problems

Liquid-Level Gage

Measurement of the depth of static liquid level is one of the simplest tests made in oil wells and, with the exception of the measurement of the total depth, probably is made more frequently than any other. Usually the measurement can be made with enough accuracy by rapidly running into a well a bailer, subsurface pressure gage, or similar tool or instrument attached to a wireline.

Measurements of depths of liquid levels have many uses, some of which require more accuracy than can be obtained by rapid lowering of a bailer or instrument. An instrument designed to locate liquid levels in wells rapidly and accurately is described in a report[33/] that contains a description and illustrations of the gage and outlines the operating procedure. Figure 4 shows the liquid-level gage in a well.

The instrument is 1-3/4 inches in diameter and approximately 6 feet in length and may be operated through 2-inch tubing. The gage consists essentially of a float that moves upward with respect to the rest of the assembly, causing a change in the flow of electric current from the surface when the liquid level is reached. The instrument has been tested under a variety of conditions and has been found to be sensitive to changes of liquid level of one-half inch. Its accuracy is limited principally by the accuracy of the wireline depth indicator used.

The liquid-level gage is covered by U.S. Letters Patent 2,610,506, issued September 16, 1952, to David B. Taliaferro, Clifford F. McClung, and Fritz G. Mueller and is assigned to the Government of the United States as represented by the Secretary of the Interior. License to build the instrument and complete working drawings may be obtained from the Secretary of the Interior.

Well-Bore Caliper

Measurement of the bore-hole diameters in oil wells has been a common practice for many years. The first well-bore caliper was designed by M. M. Kinley (U.S. Patent 2,102,080, July 2, 1937), who used the instrument in 1932 in the Glenn Pool, Oklahoma, to obtain what is believed to be the first caliper log of a drilled well. A well-bore caliper designed in the Bureau of Mines is discussed in a report[34/] that describes and illustrates the instrument and outlines the operating procedures. A bibliography is included that gives references to articles and patents on the development and use of other well-bore calipers. Figure 5 shows the Bureau of Mines well-bore caliper in a well.

33/ Hamontre, H. C., Taliaferro, D. B., McClung, C. F., and Mueller, F. G., Bureau of Mines Liquid-Level Gage: Bureau of Mines Rept. of Investigations 5060, 1954, 8 pp.

34/ Hamontre, H. C., Armstrong, F. E., and Mueller, F. G., Bureau of Mines Well-Bore Caliper: Bureau of Mines Rept. of Investigations 5092, 1954, 18 pp.

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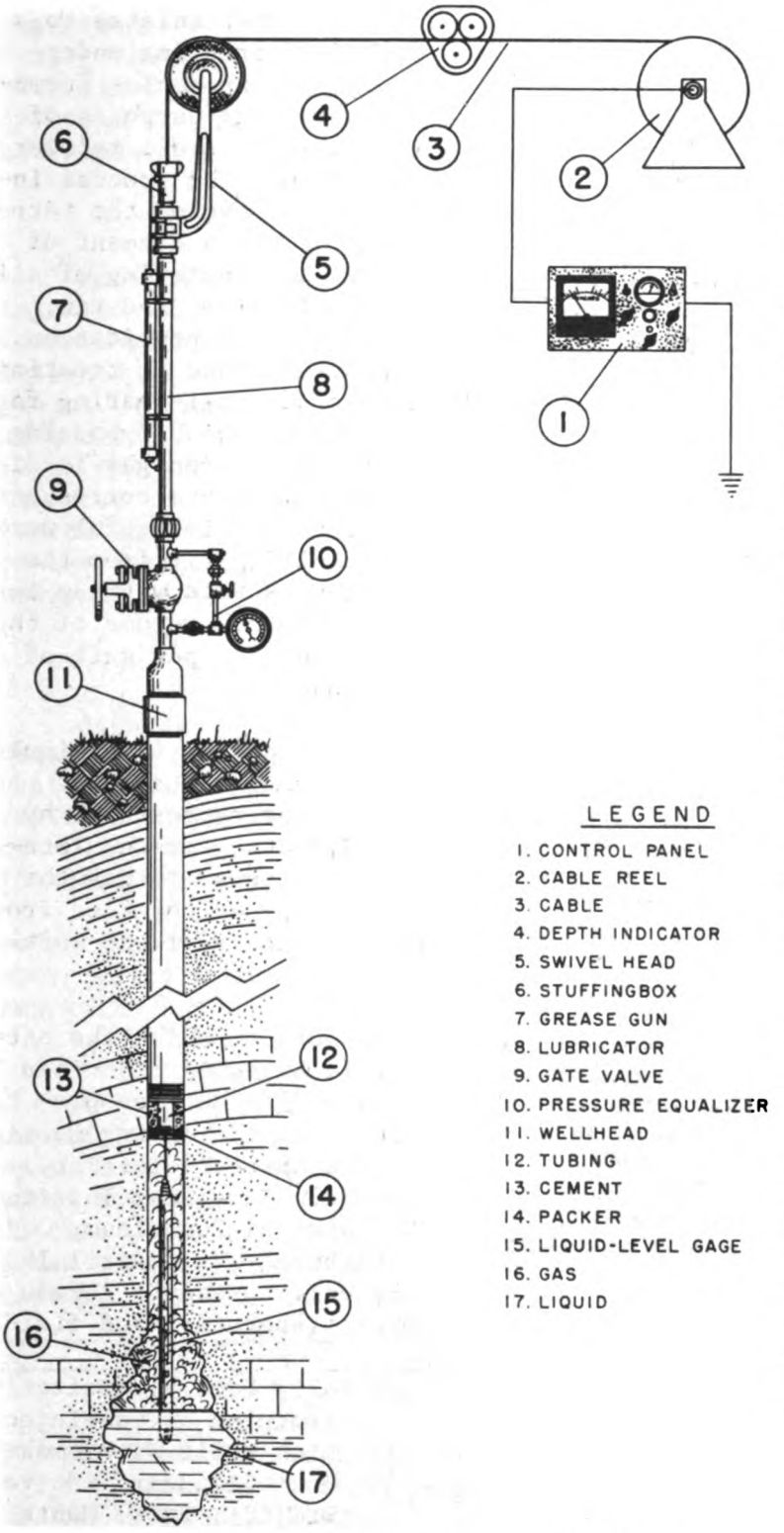

FIGURE 4. - Liquid-Level Gage in Well.

The Bureau of Mines well-bore caliper was designed to provide an instrument that could be operated through 2-inch tubing, which is used particularly in many input wells on waterflooding projects. It should find wide application elsewhere under many other conditions where it has not been possible previously to make caliper logs with the larger diameter probes used on other instruments. The caliper has three additional advantages over other instruments of this type: (1) It measures 4 radii (up to 18 inches) 90° apart with an accuracy of ± 1/4 inch; (2) the measuring arms can be opened and closed at will by remote control, and (3) it is run and operated on a single-conductor, armored electric cable (Amergraph, type 1-H-0).

The well-bore caliper is covered by U.S. Letters Patent 2,771,686, November 27, 1956, issued to Hugh C. Hamontre, Fritz G. Mueller, and Frederick E. Armstrong. The patent is assigned to the Government of the United States and has been licensed to industry. License to fabricate, sell, and use the instrument may be obtained from the Secretary of the Interior.

Selective Plugging

U.S. Patent 2,808,886, October 8, 1957, to Paul T. Bail, Bruce F. Grant, and

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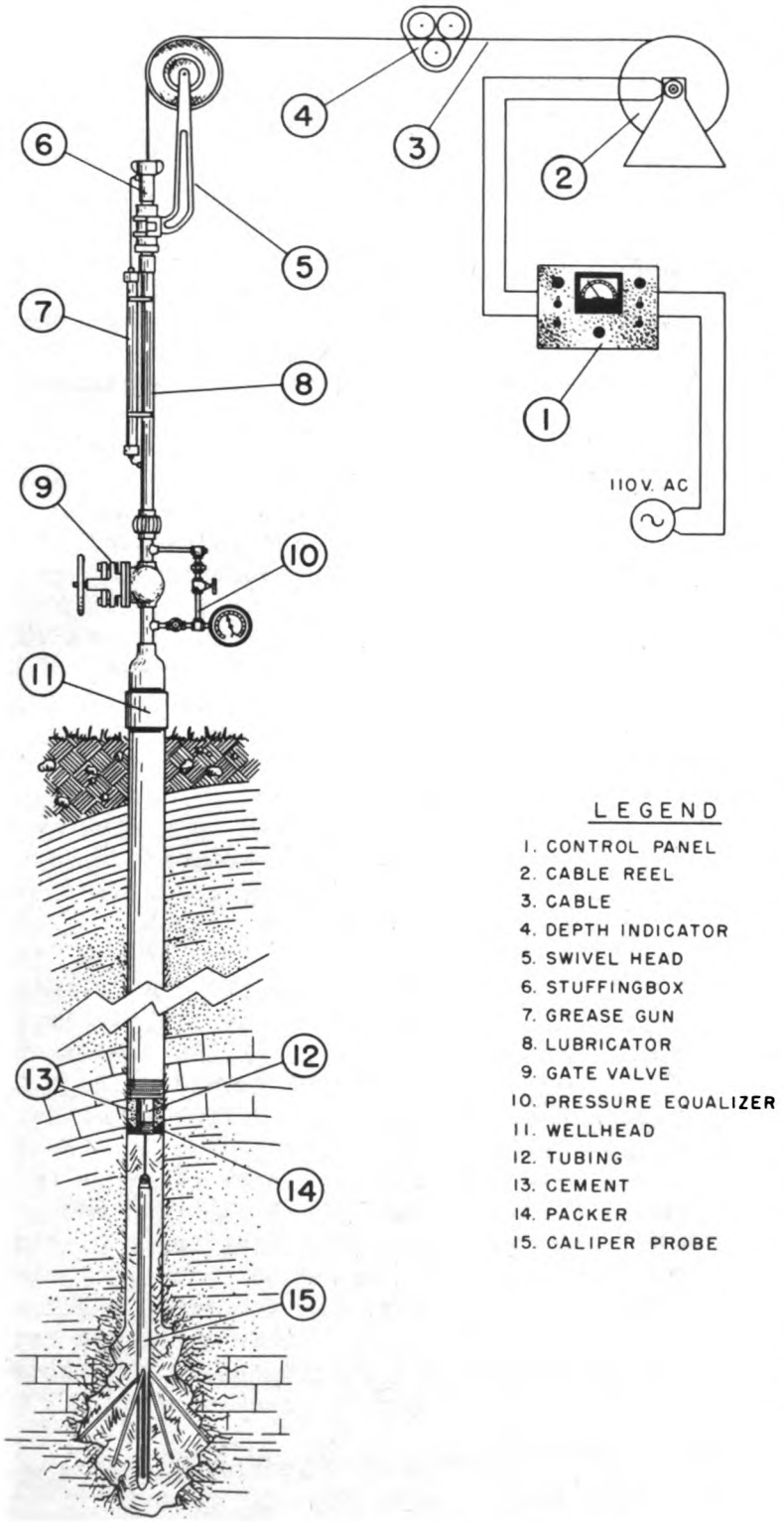

FIGURE 5. - Well-Bore Caliper in Well.

Simon Klosky, relates to a method of treating underground oil-producing formations for the purposes of increasing the oil recovery therefrom. The process involves the use of the tetrachloride of an element of the group consisting of silicon, titanium, and tin. The invention provides an improved method of treating underground oil-bearing formations in which bypassing of the injection gas is diminished, with a corresponding increase in useful work in expelling oil from the adjacent strata with an increase in the volume of the oil recovered per unit of gas injected.

The patent is assigned to the United States of America as represented by the Secretary of the Interior. License to use the method may be obtained from the Secretary of the Interior.

Work on which the patent is based is described in a paper35/ that was presented at the spring meeting of the Eastern district, American Petroleum Institute, Division of Petroleum, Pittsburgh, Pa., April 1953. The paper presents Bureau of Mines laboratory and field

35/ Bail, Paul T., Selective Plugging of Gas-Injection Wells With Smoke on a Secondary Recovery Project: Prod. Monthly, vol. 18, No. 5, March 1954, pp. 24-35.

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experiments on selective plugging of oil-reservoir sands with smoke in the Pennsylvania area. Apparatus developed, experimental procedures used, and methods of applying laboratory data to treatment of gas-injection wells with titanium dioxide smoke are described. Results of the treatment on injection and producing wells are given.

Design and Operation of Plants for Subsurface Injection

Both the design of plants in which water is to be treated for subsurface injection and the operation of the plants are important to the success of waterflooding and pressure-maintenance operations. Treating plants should be designed specifically for conditioning the water or brine to be used in the project. Watkins[36/] discusses the factors to be considered and evaluated carefully in designing a plant in which water is to be treated for subsurface injection. In general, it was concluded that a plant should be planned and operated to treat to the best advantage the specific water that will be injected in the reservoir. Close attention to the results of chemical analysis of the water and prompt and precise adjustments of mechanical equipment on the basis of those analytical results is advocated.

Tracers in Waters Used for Subsurface Injection

Accurate evaluation of reservoir-performance characteristics in the secondary recovery of petroleum by waterflooding requires use of a water tracer that may be injected into water-input wells and detected at oil-production wells to supplement data obtained from core analysis measurements. Radioactive water tracers are considered[37/] to be superior to stable tracers of water injected into oil sands. Radioactive iodine has most of the characteristics of an ideal water tracer. The short half life of artificially radioactive iodine has advantages under some conditions, but the half life (8 days) is too short where weeks or months are required for injected water to reach a producing well.

A discussion of radioisotopes in petroleum research[38/] points out that the efficiency of petroleum production by waterflooding may be increased appreciably by early detection and correction of formation heterogeneities and by improving the characteristics of the water as a flooding medium. Tracers added to water injected into input wells and detected in water entering production wells afford a means of evaluating certain reservoir conditions between wells. Characteristics of satisfactory tracers are described in the report.

36/ Watkins, J. Wade, Design and Operation of Plants for the Preparation of Water for Injection into Oil Reservoirs: Jour. Petrol. Technol., April 1955, pp. 17-23.

37/ Watkins, J. Wade, and Mardock, E. S., Use of Radioactive Iodine as a Tracer in Water-Flooding Operations: Petrol. Trans., AIME, vol. 201, 1954, pp. 209-216.

38/ Watkins, J. W., Dunning, H. N., Armstrong, F. E., Heemstra, R. J., and Hsiao, L., Radioactive Isotopes in Petroleum Production Research: Prod. Monthly, vol. 20, No. 6, April 1956, pp. 41-57.

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Laboratory Studies

Conduction of Heat

The nature of the physical and chemical processes underlying thermal methods of oil recovery are not yet well understood. One of the processes involved is the transfer of heat by conduction in oil-reservoir rocks containing moving reservoir fluids. A technical note[39] deals with heat conduction in a laboratory sand column filled with a moving hydrocarbon (propane) and therefore should contribute to the presently inadequate fund of knowledge on the overall subject.

Checking Geiger-Mueller Tubes

A test instrument for use in checking the operational characteristics of Geiger-Mueller tubes is described in an article,[40] which includes a photograph of the assembled apparatus and a diagram of the circuit for the Geiger-Mueller tube checking device. The test instrument is said to be inexpensive to construct and fully automatic in operation and to give much more accurate results than the usual manual methods. The device was designed for use with a standard commercial counting-rate meter (Berkeley Model 2810) and a 1-milliampere, moving-coil type, strip-chart recorder (Esterline-Angus).

Measurement of Surface Areas

It is generally recognized that, among the various physical factors that affect oil recovery from porous rock, interfacial forces play an important role in both the primary and the secondary phases of oil production. A Bureau paper[41] presents a modification of a projected-area method developed in the Bartlesville laboratory for direct measurement of specific surface areas of irregularly shaped particles, such as crushed quartz. It is more rapid than previously described procedures and yet is capable of comparable accuracy.

The projected-area method was modified for direct microscopic measurement of the specific surface areas of nonporous particulate matter, such as convex, irregularly shaped, crystalline particles.

Application of surface-area measurements of clays and core samples to the efficiency of oil recovery is discussed in a paper[42] that also presents the

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39/ Miller, Frank G., and Seban, Ralph A., The Conduction of Heat Incident to the Flow of Vaporizing Fluids in Porous Media: Tech. Note 319, Trans. AIME, vol. 204, Petrol. Develop. and Technol., 1955, pp. 232-234.

40/ Armstrong, F. E., Simple, Inexpensive Device Checks G-M Tube Operation: Nucleonics, vol. 14, No. 8, August 1956, pp. 79-80.

41/ Pidgeon, Frances D., and Dodd, Charles G., Precise Measurement of Particle Surface Area With the Microscope: Anal. Chem., vol. 26, No. 11, November 1954, pp. 1823-1828.

42/ Loomis, Albert G., Surface-Area Measurements of Clays and Sedimentary Rock by a Liquid-Phase Adsorption Method: Prod. Monthly, vol. 18, No. 11, September 1954, pp. 19-25.

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results of laboratory measurements of surface areas of typical samples by the general method of stearic acid adsorption. The method is based on the fact that polar molecules, such as stearic acid, are adsorbed as a monomolecular layer at the interface between solid and solution of the polar chemical. Adsorption is measured by the change in concentration of the original solution added to the clay or core sample. The weight, in mols, of stearic acid adsorbed is converted to number of molecules by the Avagadro number and finally to area, since the area of each molecule in the adsorbed layer is known.

The investigation showed that, with proper experimental procedure, surface areas of clays or core samples may be measured with precision, both gravimetrically and volumetrically, by adsorption of stearic acid from benzene or methanol solution.

Clay Studies

Baptist and Sweeney[43/] present results of an investigation to determine the clay content of typical petroleum reservoir sands in Wyoming and the effect of clay content on the permeability behavior of the sands. The permeability of samples of the sands varied when tested with air and with water, and variations were not of the same magnitude when samples of different sands were tested. The degree of permeability reduction to water, as compared with air, is shown to be a measure of the water sensitivity of the sand.

The following conclusions were drawn from these studies:

1. The water sensitivity of the reservoir sands is related to the salinity of the water and to the permeability of the sand. Water sensitivity increases with decreasing salinity and with decreasing permeability.

2. The water sensitivity of a sand is also related to the type and amount of clay-mineral constituents. The sand containing kaolins, illites, and mixed-layer montmorillonite-illite was found to be the most sensitive to water; that containing only small amounts of kaolins and illites was the least sensitive; and that containing the most kaolins and illites was intermediate.

3. The predominant clay mineral found in the three reservoir sands was kaolin. Illites were next in abundance; and a mixed-layer type, with small amounts of free montmorillonite, was found in only one of the three sands.

4. Semiquantitative analyses by X-ray diffraction methods indicated that, in many instances, only a small proportion of the fine silt and clay size was clay minerals.

Figure 6 is a photograph of the apparatus used at the Laramie Petroleum Research Center to determine the permeability of oil sands to gas, water, and

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43/ Baptist, O. C., and Sweeney, S. A., Effect of Clays on the Permeability of Reservoir Sands to Various Saline Waters, Wyo.: Bureau of Mines Rept. of Investigations 5180, 1955, 23 pp.; Chapter on Clays and Clay Minerals, Nat. Acad. Sci., Nat. Res. Coun., Washington, D. C., 1955, pp. 505-515.

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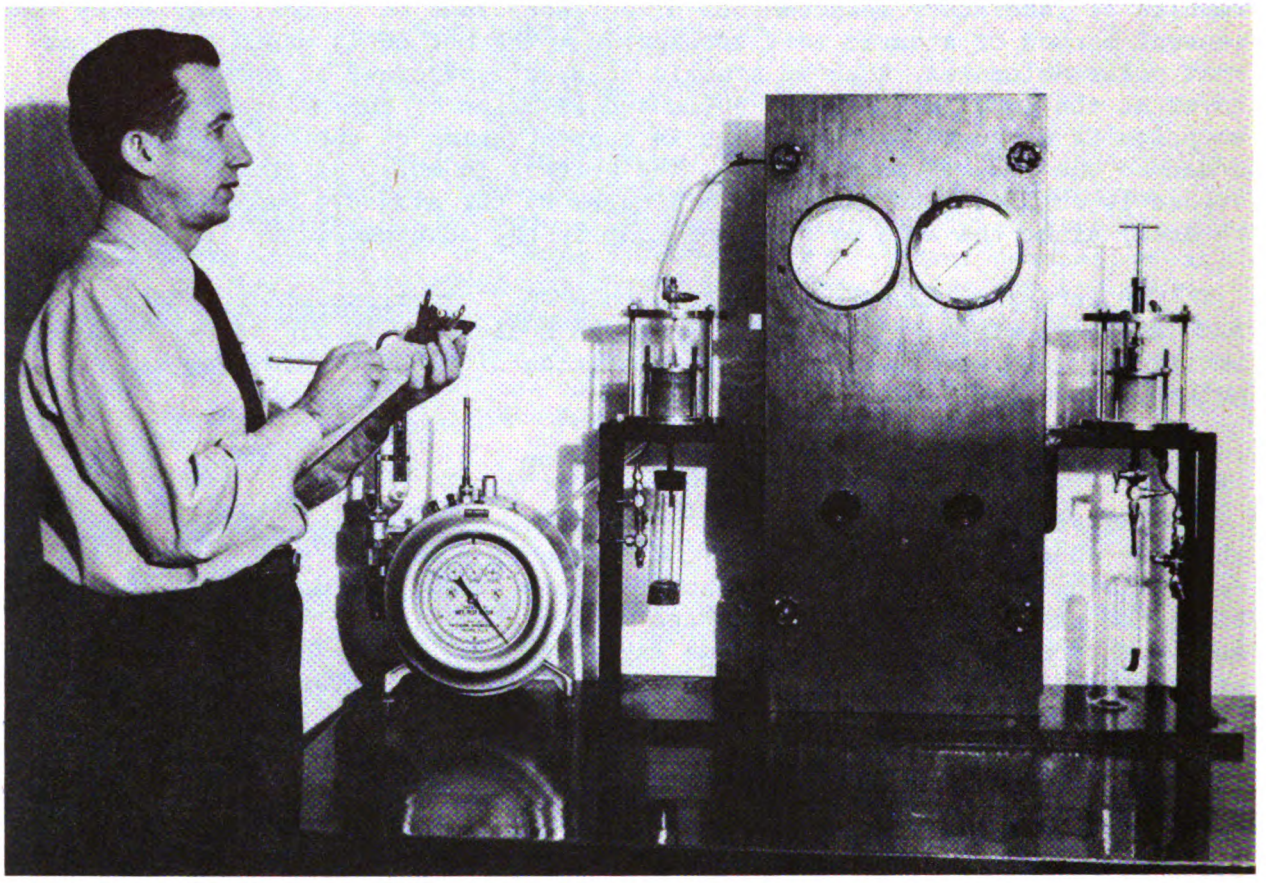

FIGURE 6. - Apparatus to Determine the Permeability of Oil Sands to Gas, Water, and Brine. Comparison of These Results Indicates the Deleterious Effect of Clays in the Sands.

brine. Comparison of these results indicates the deleterious effect of clays in the sands.

A literature survey related to clay minerals and their effect on petroleum production was made before undertaking experimental work. A brief review of the survey[44/] was published to help petroleum operators become familiar with the nature of clays and methods of minimizing the effects of water on water-sensitive sands. The paper points out that the three clay minerals of interest in the production of petroleum from reservoir sandstones are kaolinite, montmorillonite, and illite. The schematic crystal structures of these three clay minerals are illustrated, and the methods of analysis utilized in determining whether clay minerals are present in oil-bearing sandstones, and if so, the type and amount present, are described. A list of 18 references is appended.

44/ Noonan, John F., How to Identify Clay Minerals--and Why: World Oil, vol. 143, No. 7, December 1956, p. 186.

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Core and Water Analysis

Information regarding the pores or voids in reservoir rocks is vitally important in the extraction of petroleum from natural underground reservoirs, and various methods of analysis devised by petroleum technologists concerned with subsurface conditions give reasonably satisfactory information on the porosities of oil- and gas-bearing sands.

The method that has been used by the Bureau of Mines for determining the effective porosity of oil- and gas-bearing sands was devised and developed as part of the Bureau's research on fluid-energy relationships and on methods of improving the recovery of crude oil from underground reservoirs. The apparatus has been improved and made more convenient to use, but the procedure is essentially the same as that which has been in use for many years. A report[45/] describes and illustrates the apparatus and explains the procedure in detail. Results of more than 4,800 porosity determinations for oil sands in fields of 13 States are given.

Susceptibility of Reservoir Sand

Studies to develop laboratory data of the type most likely to be needed by persons studying the susceptibility of the Newcastle sand reservoir to secondary recovery methods are reported in a paper[46/] that outlines the physical properties and behavior of samples of reservoir sand in the laboratory. Laboratory methods and procedures are described, and results of clay analyses, porosity tests, permeability tests, and other factors are tabulated.

The results are not intended to describe specifically reservoir properties or behavior, but they are useful in estimating original reservoir conditions and in predicting how the conditions will be changed by injection of various fluids for secondary recovery.

Testing Waters for Subsurface Injection

Early in the development of the practice of subsurface injection of brines for disposal of and increasing the recovery of oil, it became evident that different methods of chemical treatment and different conditioning equipment would have to be devised to sustain desired injection rates into water-input wells. These changes became necessary because the highly mineralized waters produced with petroleum from deep formations became chemically unstable when pumped to the surface, because of loss of dissolved gases as pressure and temperature dropped to atmospheric, and because of contact with atmospheric oxygen at the surface.

45/ Rall, Cleo G., Hamontre, H. C., and Taliaferro, D. B., Determination of Porosity by a Bureau of Mines Method: A List of Porosities of Oil Sands (rev. of Rept. of Investigations 4548): Bureau of Mines Rept. of Investigations 5025, 1954, 24 pp.

46/ Baptist, Oren C., and Sweeney, S. A., Physical Properties and Behavior of the Newcastle Oil-Reservoir Sand, Weston County, Wyo.: Bureau of Mines Rept. of Investigations 5331, 1957, 43 pp.

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During this development period it also became evident that the standard methods of water analysis for fresh and surface waters were not suited to testing most oilfield brines because of the unstable nature of the dissolved gases present and the high concentration of minerals in solution. It was learned that water analyses to determine unstable constituents of brines quantitatively should be conducted at conditioning-plant sites.

The report on this research[47/] describes in detail methods of making corrosion tests and chemical analyses that have been used extensively and satisfactorily in a study of plants in which various surface waters and brines are conditioned for waterflooding, brine disposal, and reservoir-pressure maintenance in Kansas, Oklahoma, and north Texas. The tests and analyses described were designed and adapted for use in the field in determining the relative corrosive and plugging tendencies of waters from various sources conditioned by different methods. Although the described methods were developed and used in testing oilfield waters in the Midcontinent oil-producing area of the United States, these same methods should be equally applicable to testing oilfield or highly mineralized waters throughout the world.

Oxygen Dissolved in Oilfield Brines

One of the problems encountered by Bureau of Mines engineers in field studies of the corrosivity of oilfield brines is the difficulty of making reliable quantitative determinations of dissolved oxygen in the brines. A paper[48/] describes an instrument that offers a number of refinements over other equipment. The authors conclude that the instrument, using a rotating platinum microelectrode, is capable of accurate, reproducible results when properly applied by the operator. Careful workmanship in the preparation of the electrode and diligent application is necessary if accuracy within about 5 percent is desired. The portability of the amperometric instrument permits the analyst to make the determination at field sampling points.

Resistivity of Formation Water

A report prepared by engineers of the Bureau of Mines under cooperative agreements with the Arkansas Oil and Gas Commission and the Louisiana Department of Conservation[49/] points out that knowledge of the resistivity of the water in an oil-producing formation is essential for fullest utilization of the electric log. Information presented in the paper eliminates the need of

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47/ Watkins, J. W., Analytical Methods of Testing Waters to Be Injected Into Subsurface Oil-Productive Strata: Bureau of Mines Rept. of Investigations 5031, 1954, 29 pp.

48/ Armstrong, F. E., Heemstra, R. J., and Kincheloe, G. W., Amperometric Instrument for Quantitative Determination of Oxygen Dissolved in Oilfield Brines: Anal. Chem., vol. 27, August 1955, pp. 1296-1300.

49/ Hawkins, Murphy E., and Moore, J. L., Electrical Resistivities of Oilfield Brines: Petrol. Eng., vol. 28, No. 7, July 1956, pp. B-80--B-92; Petrol. Eng., vol. 28, No. 9, August 1956, pp. B-104, B-109, B-110, B-113.

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estimating formation-water resistivity and should result in increased accuracy of quantitative electric log interpretation. Water-resistivity data also are useful for determining casing leaks in wells and for identifying the geological age of formations.

Resistivity of water is defined as the property of water that restricts the flow of an electric current. The unit generally used in electric log practice is the ohm-meter (ohm-m.). This unit expresses the resistance in ohms of 1 cubic meter of water to the flow of a uniform electric current parallel to one side of the cube. Water resistivity may also be expressed in ohm-meters squared per meter (ohm-m.^{2}/m.), or in ohm-centimeters (ohm-cm.).

Resistivities of formation waters from seven oil-producing counties in southern Arkansas and 21 parishes in northern Louisiana are included in the two parts of the report. Locations of oilfields from which water samples were obtained are shown on an index map of each county or parish. Average water resistivities, tabulated by counties and parishes, fields, and producing formations, are shown in tables.

Water resistivities either were measured with a portable resistivity meter or calculated from mineral analyses.

Recovery Efficiency of Waterflooding High-Viscosity Oils

One of the important problems that confronts oil producers in appraising the possibilities of secondary recovery in many California fields is the effect of the viscosity on oil recovery by waterflooding. In January 1954, 554 fields and/or pools in the State produced a total of 1 million barrels daily, and 138 of these pools produced approximately 267,000 barrels daily of heavy crude oils having gravities heavier than 20° API. Many of these fields were nearing the end of their economic life as primary producers and still had high residual-oil saturations--a favorable factor in waterflooding. The problem was whether enough oil could be recovered from these fields by waterflooding to make the operation economically successful.

Fried[50/] presents the results of 11 laboratory waterflooding experiments in which oils of seven different viscosities, ranging from approximately 1-1/2 to 850 centipoises, were displaced from an alundum core by brine. All controllable variables except oil viscosity were held as constant as practicable throughout the series of tests. The experiments indicate the advisability of intensive study to determine, especially in pools of high API gravity and otherwise susceptible to waterflooding, the advantages of instituting a flood early in the history of the field before the reservoir oil is made more viscous by loss of solution gas. The results of the investigation primarily serve to show the relative importance of oil viscosity on recovery by waterflooding.

50/ Fried, A. N., Effect of Oil Viscosity on the Recovery of Oil by Water Flooding: Bureau of Mines Rept. of Investigations 5115, 1955, 34 pp., 16 figs.

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Domestic Substitutes for Quebracho

For its supply of quebracho for use in conditioning oil-well drilling fluids and in tanning leather, the United States relies wholly on importations from Argentina and Paraguay, as there is no domestic source of supply.

In a search for quebracho substitutes 70 materials, comprising both natural and synthetic substances ranging from chemically processed "chicken feathers" to South African "wattle-bark" extract, were tested at the San Francisco Petroleum Research Laboratory. Most of the natural materials were agricultural and wood byproducts, and most of the synthetic materials were of the detergent type. Although none of materials tested was found to be equivalent to quebracho in effectiveness, especially on a pound-for-pound basis, some materials approached quebracho in controlling the properties of three drilling fluids under most conditions. Caraway[51] presents the results of laboratory evaluation tests showing the relative merits of 15 substitute materials as to their effect on the viscosity and filter properties of three drilling fluids, and the resistance of these fluids to sodium chloride contamination and to high-temperature deterioration. In addition, the paper includes graphical data comparing the effectiveness of the materials believed to have most practical interest. Included also is a discussion of the availability of some of the more effective substitutes. The evaluation tests are described in the paper, and results are presented in three tables and six figures.

Results of the tests indicated that from an overall viewpoint lignite product No. 1 was the best of the quebracho substitutes tested by the Bureau of Mines.

Surface Forces in Petroleum Production

During the past few years it has become increasingly evident that further improvement in secondary-recovery methods will depend on proper applications of the principles of surface chemistry to the field of secondary-recovery research. The extensive surface areas and porous natures of petroleum-reservoir materials magnify surface forces to such an extent that they may become controlling factors in removing oil from petroleum reservoirs.

Fluid-Flow Phenomena

Better understanding of the fundamental laws governing fluid flow through petroleum reservoir rocks is a key to engineering developments capable of improving the efficiency of petroleum-production methods. The flow of fluids in a natural petroleum reservoir usually involves a multiphase system of gases and liquids flowing through heterogeneous porous materials. The understanding of a simple, homogeneous system is a prerequisite to the understanding of the more complicated systems found in petroleum reservoirs.

51/ Caraway, W. Hodge, Domestic Substitutes for Quebracho in Oilwell Drilling Fluids: Petrol. Eng., vol. 25, No. 12, November 1953, pp. B-81--B-83, B-86, B-88, B-89, B-92.

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A fundamental study of the effects of wettability on the flow of homogeneous fluids through consolidated porous materials was completed.52/ The effects of wettability on fluid distribution in pores that had a single opening and in unique intersecting-capillary systems were observed. Correlations of the permeability data with microscopic observations of these systems indicate that differences in wettability may affect fluid distribution, which in turn affects permeability if complete liquid saturation of the porous media is not achieved.

Detergents in Petroleum Production

The large amount of crude oil remaining in producing formations despite the most efficient current production practices is a constant challenge to research scientists of Government and industry alike. Several secondary-recovery methods have been widely used, and many more have received attention.

One of the most direct methods of changing the surface forces existing in petroleum reservoirs is the use of surface active agents (detergents) in flood waters. Accordingly, a comprehensive research program was initiated to investigate the practical and fundamental aspects of detergency in petroleum production.

Nonionic Detergents

Development of new detergents, particularly of the nonionic type, offers new possibilities in this field of study. The results of investigations by Bureau of Mines personnel involving four series of nonionic detergents have been reported.53/ This study showed that some of the detergents tested were highly effective for removing crude oil from unconsolidated sand.

Centrifugal Testing

The centrifugal method developed for this study has found acceptance in several industrial laboratories. Therefore, an intensive study was made of the test variables.54/

The test results were found to be relatively insensitive to variations in temperature, period of contact between oil and sand, method of preparing samples, and crude-oil composition. The method can be adjusted to give the desired rapidity and discrimination by varying oil saturation, sand-particle size, centrifugal force, or violence of agitation.

52/ Johansen, R. T., and Dunning, H. N., Homogeneous Fluid Flow Through Consolidated Porous Media: Jour. Colloid Sci., vol. 12, No. 1, February 1957, pp. 68-79.

53/ Dunning, H. N., Gustafson, H. J., and Johansen, R. T., Displacement of Petroleum From Sand Surfaces by Solutions of Polyoxyethylated Detergents: Ind. Eng. Chem., vol. 46, No. 3, March 1954, pp. 591-596.

54/ Dunning, H. N., Hsiao, Lun, and Johansen, R. T., Variables in Centrifugal Testing of Petroleum Displacement by Detergent Solutions: Ind. Eng. Chem., vol. 47, No. 10, October 1955, pp. 2147-2152.

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The centrifugal method was used to screen examples of the numerous available detergents.[55] The effectiveness of these detergents in crude-oil displacement was correlated with their physical properties, such as surface tension, cloud point, and detergent type.

Displacement Efficiencies

Results of studies of displacement efficiencies and properties of 105 detergents are tabulated in a paper[56] that describes the equipment and methods used and explains the significance of various factors of detergency as applied to displacement of petroleum from sand surface. A list of references to the literature is appended to this paper.

Nonionic detergents, because of their high displacement efficiencies in a pure form or in built formulations, appear to be the most promising as waterflooding additives. Furthermore, the nonionic molecule is compatible with substances common to injection and formation water.

The most effective use of detergents in oil recovery and cleanout procedures requires understanding of their basic properties. Fundamental studies have been made of pertinent detergent properties.

Surface-Tension Balance

A chainomatic balance was modified and equipped with a novel thermostat-elevating platform[57] for measuring surface tension by the du Nouy ring method.

Adsorption of Detergents

Detergents prepared by condensation of ethylene oxide with an alkylphenol have attained widespread industrial usage. Because the mole ratio of ethylene

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55/ Dunning, H. N., Hsiao, Lun, and Johansen, R. T., Displacement of Petroleum From Sand by Detergent Solutions: Bureau of Mines Rept. of Investigations 5020, 1953, 19 pp. Oil Displacement by Detergents: Petrol. Eng., vol. 26, No. 1, January 1954, pp. B-82--B-90. Soap Washes Oil Out of Sand: Oil Gas Jour., vol. 53, No. 15, Aug. 16, 1954, pp. 139-149.

56/ Johansen, R. T., Dunning, H. N., and Beaty, Jeanne W., Detergent for Petroleum Displacement: Soap and Chem. Specialities, vol. 31, October 1955, pp. 41-46; November 1955, pp. 53-56. Petroleum Displacement by Detergent Solutions: Mineral Industries Experiment Station Bull. 68, 19th Tech. Conf. on Petroleum Production, Nov. 16-18, 1955, Pennsylvania State University, University Park, Pa., pp. 85-92. Petroleum Displacement by Detergent Solutions: Prod. Monthly, vol. 20, No. 4, February 1956, pp. 26-35.

57/ Dunning, H. N., and Johansen, R. T., A Combination Thermostat and Elevating Platform for the Surface-Tension Balance: Rev. Sci. Instr., vol. 24, 1953, p. 1154.

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oxide to phenol can be varied continuously above a value of 1, detergents with a wide range of properties can be prepared readily. Because of the extremely large surface areas of petroleum-producing formations, adsorption of detergents may cause their use to be economically prohibited.

The adsorption of six members of series based on nonylphenol and of three members of the octylphenol series was investigated with a fine quartz powder.58/ The data afford comparisons of the effects of composition on adsorption and allow generalizations of the behavior of similar detergents.

The adsorption of detergents on sand is of primary concern in their use as additives in the secondary recovery of petroleum by waterflooding. Such adsorption, if extensive and irreversible, would result in a great enough detergent loss to affect adversely the economical use of such additives. Previous investigations in the Bartlesville laboratory had shown that nonionic detergents were generally effective in displacing petroleum from sand surfaces. A comparative study of the adsorption of nonionic alkyl aryl polyoxyethylated detergents on sand by different methods was made to determine the fundamental mechanisms of nonionic detergent adsorption.59/ The techniques used in the study were: (1) The radiotracer method, with which the C^{14}-tagged ethylene oxide chains (hydrophilic) were traced; (2) the spectrophotometric method, with which the phenol groups (hydrophobic) were determined; and (3) the surface tension method, with which the surface-active species were determined.

Critical Micelle Concentrations

In another fundamental detergent study60/ the critical micelle concentrations of nonionic detergents composed of nonylphenol and various ethylene oxide chain lengths were determined by the surface tension method. Critical micelle concentrations increase with ethylene oxide chain length and decrease with increasing electrolyte concentration. The term "critical micelle concentration" may be defined as the concentration at which the detergent reaches its maximum effectiveness. Critical micelle concentrations increase with ethylene oxide chain length and decrease with increasing electrolyte concentration. Of practical importance, this study showed that these kinds of nonionic detergent may be used in strong oilfield brines as well as in fresh water and indeed reach their maximum effectiveness at lower concentrations in the brines.

58/ Dunning, H. N., Adsorption of Polyoxyethylated Detergents on Quartz: Chem. Eng. Data Series, vol. 2, No. 1, 1957, pp. 88-91.

59/ Hsiao, Lun, and Dunning, H. N., A Comparative Study of Non-Ionic Detergent Adsorption by Radiotracer, Spectrophotometric, and Surface Tension Methods: Jour. Phys. Chem., vol. 59, April 1955, pp. 362-366.

60/ Hsiao, Lun, Dunning, H. N., and Lorenz, P. B., Critical Micelle Concentrations of Polyoxyethylated Detergents: Jour. Phys. Chem., vol. 60, May 1956, pp. 657-660.

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Field Tests

Because results of only a few field tests of detergents as floodwater additives had been published, a large-scale field test was made in a relatively new waterflood project in Washington County, Okla.[61/]

After 1 year of testing detergents in the Grover waterflood of northeastern Oklahoma, these results were obtained:

1. Effective formation permeability increased, and skin factors improved in most of the wells tested, as a result of detergent injection.

2. Increased injectivity followed detergent injection, but this was temporary. Skin factors of some of the wells showed permanent improvement.

3. Injectivity of comparatively impermeable water-input wells increased more during detergent injection than did loose or controlled wells. This indicates that zones of the oil-productive sand previously either inaccessible or impermeable to injection water were penetrated by the detergent solution.

4. Some increases in oil production were observed, but little definite increase in the oil-production rate or lessening of normal production-decline rate may be cited as a result of detergent injection. Increases in oil production resulting from increased water-injection rates may not be observable for some time.

The results of these basic and applied laboratory and field studies show that dilute solutions of carefully selected detergents remove considerably more oil from unconsolidated sand than does water. Their efficiency in consolidated media is less conclusively demonstrated and is very sensitive to operational variables. Several of the detergents tested are effective for increasing the rate of water injection into oil-producing formations and for cleaning water-input wells in waterflood projects.

Porphyrins in Petroleum

The tenacity with which petroleum clings to reservoir rock surfaces is due primarily to the minor constituents of petroleum. These constituents are more polar than are hydrocarbons because their water-soluble groups contain sulfur, oxygen, and nitrogen in various forms. The properties of these minor constituents, therefore, are important in determining the kind and efficiency

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61/ Dunning, H. N., Johansen, R. T., Walker, C. J., Powell, J. P., and Watkins, J. W., Field Test of a Detergent in Oil Recovery: Min. Ind. Exper. Sta. Bull. 68, 19th Tech. Conf. on Petroleum Production, Pennsylvania State University, University Park, Pa., Nov. 16-18, 1955, pp. 21-27. Field Test of a Detergent in Oil Recovery: Prod. Monthly, vol. 20, No. 5, March 1956, pp. 29-35. Have You Tried a Waterflood Detergent?: World Oil, vol. 143, No. 4, September 1956, pp. 196-204.

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of detergents or other agents required for the displacement of petroleum from reservoir surfaces. Recent studies by Bureau of Mines and industrial scientists indicate that nitrogenous substances are of major importance in causing petroleum to adhere to rock surfaces. One type of nitrogenous substances (the porphyrins) was studied extensively at the Bartlesville Petroleum Research Center in Bartlesville, Okla. These studies resulted in the accumulation of considerable data on the properties of the porphyrins and their effects on the exploration for, production of, and refining of petroleum.

Porphyrin-Metal Complexes

The porphyrins and their metal complexes may be readily recognized by physicochemical methods. The vanadium-porphyrin complex, indigenous to many bituminous substances, is remarkably stable. Therefore, these complexes serve as natural "tracers"; observations of their occurrence and properties permit an insight into some of the mysterious processes of petroleum formation.

Propane precipitation results in separation of a considerable amount of the metal-porphyrin complexes from the refined portion of the oil because the metal-porphyrin complexes are mainly associated with the asphaltic portion of petroleum. Extracts relatively rich in metal-porphyrin complexes are obtained when propane precipitation is followed by extraction of the asphalt with solvents of increasing polarity. This method was used[62/] to isolate vanadium- and nickel-porphyrin complexes from California crude oils. Nickel- and vanadium-porphyrin complexes were isolated also from the dissolved portion resulting from the propane precipitation of an asphaltic Midcontinent crude oil.[63/] The isolation procedure involved extensive chromatography with silica gel and alumina columns. The vanadium- and nickel-porphyrin complexes were volatilized at a pressure of about 10 microns at temperatures from 250°-300° C. Molecular distillation methods offer a promising way of purifying the porphyrin complexes, and may be useful for purifying the free porphyrins as well.

Oil Shale

The high nitrogen content of its organic constituents indicated that oil shale might be a rich source of porphyrin complexes. Therefore, a Colorado oil shale was extracted successively with solvents of increasing polarity.[64/] Correlations of the porphyrin and total nitrogen contents of oil-shale extracts with their interfacial activities indicate the importance of these substances in determining the interfacial properties of the extracts. The presence of metal-porphyrin complexes in these oleaginous deposits is indicative of the biological origin of oil shales.

62/ Dunning, H. N., Moore, J. W., and Myers, A. T., Properties of Porphyrins in Petroleum: Ind. Eng. Chem., vol. 46, No. 9, September 1954, pp. 2000-2007.

63/ Dunning, H. N., and Rabon, N. A., Porphyrin-Metal Complexes in Petroleum Stocks: Ind. Eng. Chem., vol. 48, No. 5, May 1956, pp. 951-955.

64/ Moore, J. W., and Dunning, H. N., Interfacial Activities and Porphyrin Contents of Oil-Shale Extracts: Ind. Eng. Chem., vol. 47, No. 7, July 1955, pp. 1440-1444.

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Paper Chromatography

An interesting development in porphyrin research was the successful application and extension of paper chromatographic methods for the resolution of the porphyrin aggregate (free of metals) of a California crude oil into several distinct groups.65/ Several of the groups consisted of decarboxylated porphyrins. In addition to a large amount of decarboxylated porphyrin material, the porphyrin material of two heavy asphaltic oils from California (Santa Maria Valley) and Oklahoma (Tatums) contained about 8 percent of carboxylated porphyrins.

The widespread occurrence of metal-porphyrin complexes in bituminous materials is definite evidence of the biological origin of crude oil. The carboxylated porphyrin content of some crude oils indicates that these oils, and presumably many others, have a low-temperature history.

These results offer considerable support for the current theories that petroleum is formed slowly in marine or brackish environments from marine and terrestrial plant and animal matter and that the asphaltic constituents of crude oils are of primary formation; during the evolution of the oil these simplify to form the clean, paraffinic oils commonly associated with older formations.

TRANSPORTATION AND STORAGE OF NATURAL GAS

Bureau of Mines research on the factors of transportation and storage of natural gas is done in cooperation with the American Gas Association. This cooperative arrangement began in 1946 and has been renewed annually.

Subsurface Pressures in Gas Wells

As a part of the Bureau's study of the flow of natural gas through pipe and commercial pipelines, a report66/ on transmission factors for the flow strings of gas wells was prepared to fulfill the need for more accurate means of calculating subsurface pressures in gas wells. Engineers use transmission factors in flow equations to compute subsurface pressures in flowing gas wells from measured well-head pressures. Knowledge of these subsurface pressures is necessary for determining the productivity of gas wells from "back-pressure" tests.

Transmission factors for the flow strings of gas wells were determined by tests on wells in six fields of Oklahoma, Texas, and Louisiana. Data were

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65/ Dunning, H. N., and Carlton, J. K., Paper Chromatography of a Petroleum Porphyrin Aggregate: Anal. Chem., vol. 28, No. 9, September 1956, pp. 1362-1366.

66/ Smith, R. V., Williams, R. H., and Dewees, E. J., Measurement of Resistance to Flow of Fluids in Natural Gas Wells: Petrol. Trans. AIME, vol. 201, 1954, pp. 279-286; Jour. Petrol. Technol., vol. 6, November 1954, pp. 41-48.

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collected on 14 gas wells while gas was flowing through 1-1/4-, 2-, 2-1/2-, and 3-inch tubing and 5-1/2- and 7-inch casing.

Flow of Natural Gas in Pipelines

A Bureau of Mines Monograph[67/] presents the results of tests conducted on experimental pipelines and describes those lines and the related test equipment. It also includes formulas and data that operating and design engineers will find useful in practical application of the results of the investigation.

Transmission factors for turbulent flow of natural gas were determined for experimental pipelines constructed of 2-, 4-, 6-, and 8-inch seamless pipe, 8-inch welded pipe, and specially prepared, 3-inch superfinished pipe. The superfinished pipeline was stainless steel, the internal surface of which had been honed and polished to a "mirror"-smooth surface. Reynolds numbers for these determinations of friction factors ranged from a low of 49,900 in the 2-inch seamless pipeline to a high of 36,000,000 in the superfinished pipeline. The Reynolds number is a dimensionless ratio commonly used to characterize the conditions of fluid flow in circular pipes.

The transmission factors for the various experimental pipelines were analyzed, and relationships were established between transmission factor and the pertinent variables--Reynolds number, absolute roughness, and internal radius of pipe. All data taken on the superfinished pipeline, when the internal surface was clean, showed that the transmission factor was influenced only by Reynolds number.

Dewpoint Recorder

The development of an instrument to record the water-vapor content or dewpoint of natural gases in pipelines is described in a paper[68/] that points out that a means of continuously measuring the water-vapor content of natural gas had long been recognized as one of the needs of the natural gas industry. This was brought out forcibly when the industry began to realize that water in natural gas pipelines could cause trouble by the formation of gas hydrates. By keeping the gas flowing through the transmission lines dry, formation of gas hydrates could be avoided, but a means was needed of knowing just how dry the gas was.

During a cooperative study of gas hydrates by the American Gas Association and the Bureau of Mines a manually operated dewpoint instrument was developed and used for measuring the dewpoint of gases. The need for an instrument that would give a continuous record of the dewpoint or water-vapor

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67/ Smith, R. V., Miller, J. S., and Ferguson, J. W., Flow of Natural Gas Through Experimental Pipelines and Transmission Lines: Bureau of Mines Mono. 9, 1956, 89 pp. May be obtained only from the American Gas Association, 420 Lexington Avenue, New York 17, N. Y.

68/ Deaton, W. M., Measurement of Water Vapor in Natural Gas: Petrol. Eng., vol. 25, No. 10, September 1953, pp. D-27--D-34.

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continued, and development of a recording instrument for the purpose was undertaken. This work resulted in the development of an instrument that has proved to be of practical value to the natural gas industry. It is suitable for recording the water-vapor content of natural gas when the dewpoint is not lower than -20° F. The upper limit of water-dewpoint temperature detection is limited only to that of the ambient temperature. The article describes the principle of operation of the dewpoint recorder in detail.

Another report on the dewpoint recorder[69/] presents details on the construction, operation, performance, and maintenance of the instrument.

The instrument is covered by U. S. Patent 2,629,253, which is assigned to the United States of America as represented by the Secretary of the Interior, in whose hands the licensing and manufacture of the instrument lie. License to manufacture has been granted, and the instrument is available for purchase from the manufacturer.

Underground Storage of Natural Gas

An important report covering a study of an oil reservoir depleted by the primary production procedure that had been converted to a gas-storage reservoir was presented at the American Gas Association Gas Supply, Transmission and Storage Conference, May 10-11, 1956, at Chicago, Ill.[70/] The primary interest in making the study was to determine the probable additional recovery of oil by this new type of secondary-recovery procedure and to establish a procedure for calculating the gas-storage capacity of the reservoir.

The New York City Oilfield, Clay County, Tex., was the object of the study. The Lone Star Gas Company acquired the reservoir in 1952 for underground storage of gas. After all abandoned wells had been replugged and wells reconditioned for the storage project, the reservoir was repressured with natural gas.

Two major conclusions were drawn from the study: (1) Selection of the respective positions of injection and producing wells on the storage reservoir structure may affect materially the secondary oil recovery, and (2) more oil will be recovered by repeated gas injection and withdrawal in storage operation than by conventional gas cycling. This study pointed the way to an efficient secondary-recovery process for deep-seated reservoirs and proved valuable for pressure-maintenance operations using natural gas.

69/ Deaton, W. M., and Barker, P. M., Dewpoint Recorder for Natural Gases, Summary Report--AGA: April 1956, 20 pp. May be obtained only from the American Gas Association, 420 Lexington Avenue, New York 17, N. Y.

70/ Cook, A. B., Coulter, R. H., Jr., Spencer, G. B., Chin, Tim, and Elliott, W. C., Jr., Secondary Recovery From Semidepleted Oil Reservoirs Converted to Gas-Storage Operations: AGA Pamph. GSTS-56-2, 21 pp., Available only from American Gas Association, 420 Lexington Avenue, New York 17, N. Y.

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CHEMISTRY AND REFINING OF PETROLEUM

The Bureau's research on the chemistry and refining of petroleum is directed toward determination of chemical and physical characteristics of the economically important crude oils and their derived products, and study of the stability, combustion rates, and utilization of the products. These studies, and investigations of chemical and physical changes caused by low-temperature oxidation, combustion processes, or other environmental factors, lay the foundation for better processing and use. As a result, greater benefit will be obtained from each unit of product.

The Bureau's work also is planned to establish a firmer basis of chemical, physical, and engineering knowledge for the manufacture of substitutes for petroleum products by synthesis of basic petroleum components from oil shale and other raw materials.

The functions of the Bartlesville Station in the field of chemistry and examples of the means whereby chemistry is applied to the problems of the petroleum industry are described in a brief review.71/ The author states that current research by Bureau of Mines chemists and chemical engineers is providing information that is helpful in solving problems, such as separation and identification of sulfur compounds in crude oil, gum formation in liuqid fuels, suitability of various types of water for waterflooding, and thermodynamic properties of hydrocarbons and related compounds.

Bureau of Mines Bulletin 556 has a chapter on Petroleum and Natural Gas72/ that gives an historical account of the development of petroleum and natural gas as an asset to mankind and describes the operations of the multitude of organizations and individual operators who conduct the activities of the industry.

The chapter is divided into sections on: (a) Background, (b) outlook, (c) problems, and (d) a bibliography of 81 references to sources of further information. The chapter is equally interesting to the layman and technologist because of the scores of significant items about current production, reserves, transportation, and the many uses of petroleum and natural gas.

A brief article73/ outlines the principal factors in the development of industry in the four-State area: Montana, Idaho, Wyoming, and New Mexico. Its economy is based mainly upon agriculture, and very little manufacturing is done. Raw materials are abundant, and with the exception of Idaho, fossil fuels for power or for use also as raw materials are widespread.

71/ Smith, H. M., What Chemists and Chemical Engineers are Doing at the Petroleum Experiment Station: Chemist, vol. 32, No. 10, October 1955, pp. 369-373.

72/ Cattell, R. A., and others, Petroleum and Natural Gas; a chapter from Mineral Facts and Problems: Bureau of Mines Bull. 556, 1956, 80 pp.

73/ Murphy, W. I. R., Introduction to Resources for the Chemical Industry in the United States; Part I. Rocky Mountain States: Ind. Eng. Chem., vol. 45, No. 11, November 1953, pp. 2423.

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A paper published by the Division of Business and Economic Research, College of Commerce and Industry of the University of Wyoming,74/ gives pertinent data on 12 petroleum refineries that were operating in Wyoming at the time the article was written. Refining trends, research at refineries and at the Bureau of Mines Laramie Petroleum Research Center, and the outlook for the petroleum-refining industry of Wyoming are discussed. The author concludes that the petroleum-refining industry of Wyoming may be expected to grow as the increased population of the area and greater use of petroleum products create demands.

The article notes that two refineries with a combined daily rated capacity of 10,100 barrels of crude oil were to be discontinued in 1956, as a consequence of the trend toward concentration of refineries in large plants and elimination of the smaller ones. This trend is illustrated by the fact that in 1936 Wyoming had 24 refineries operating, with a combined capacity of 45,000 barrels a day, in contrast to 12 refineries in 1956 processing more than twice as much oil.

Analyses of Crude Petroleum

Bureau of Mines Routine Method

Analysis of samples of crude petroleum from important fields of the United States and throughout the world has been a major project of the Division of Petroleum since the Bureau of Mines was established in 1910. More than 6,000 samples of crude petroleum from fields in the United States and foreign countries have been analyzed by the Bureau of Mines routine method,75/ which has been used for more than 25 years without fundamental change.

Correlation Index

Use of the Bureau of Mines correlation index76/ to compare analyses made by the Bureau of Mines routine method on samples of crude petroleum is described in a brief article,77/ which illustrates the procedure with reference to an analysis of a sample of East Texas crude oil by the Bureau of Mines routine method. Correlation index patterns for five typical crude oils are presented graphically.

74/ Ball, John S., Petroleum Refining Industry of Wyoming: Wyoming Trade Winds, vol. 1, No. 4, July 1956, Laramie, Wyo., pp. 1-6.

75/ Smith, N. A. C., Smith, H. M., Blade, O. C., and Garton, E. L., The Bureau of Mines Routine Method for the Analysis of Crude Petroleum. I. The Analytical Method: Bureau of Mines Bull. 490, 1951, 82 pp.
Wenger, Welton J., and Ball, John S., Analytical Distillation of Crude Oils at High Altitudes by the Bureau of Mines Routine Method: Bureau of Mines Rept. of Investigations 4517, 1949, 9 pp.

76/ Smith, H. M., Correlation Index to Aid in Interpreting Crude-Oil Analyses: Bureau of Mines Tech. Paper 610, 1940, 34 pp. (out of print).

77/ Smith, H. M., and Ball, John S., Crude Oil Characterization by the Bureau of Mines Routine Method: Petrol. Eng., vol. 26, No. 6, June 1954, pp. C-12--C-14.

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Oklahoma

A report[78] gives summaries of 61 analyses of crude oils from some Oklahoma fields. Many of the analyses have been published in previous reports of the Bureau of Mines. The article contains complete Bureau of Mines routine analyses of samples from the Southwest Antioch, Burbank, West Edmond, and Oklahoma City fields of Oklahoma. Correlation index curves for four Oklahoma crude oils and one each from East Texas and Bradford (Pennsylvania) are given.

Summaries of data showing sources and general characteristics of the 61 samples and analytical and computed data are tabulated.

Wyoming and Montana

An article on characteristics of crude oils from Big Horn Basin fields[79] summarizes data showing sources and general characteristics of 103 samples of crude oils, from fields in the Big Horn Basin of Wyoming and Montana, that have been analyzed by the Bureau of Mines routine method and a complete routine analysis of a sample from the Tensleep sandstone in the Bonanza field, Big Horn County, Wyo. The analyses represent most of the fields and productive formations within the basin.

All low-sulfur oils discussed in this report were produced from Cretaceous formations, whereas all oils with more than 0.5 percent sulfur were produced from formations older than Cretaceous. Further correlations between types of oil and geological source are suggested in the report.

A map of oilfields and gasfields in the Big Horn Basin and five graphs (figures) showing correlation index patterns representing oils from Cretaceous, Triassic, Permian, Pennsylvanian, and Mississippian formations are included. Use of the correlation index to compare different crude oils, or to compare one boiling range of a crude oil with other portions of the same oil, is explained.

Beaver Lodge Field, North Dakota

Discovery of the Beaver Lodge field in the Williston structural basin in 1951 was important because of the size of the field and because it was the forerunner of development of a large new oil-producing area. An article[80] deals specifically with a sample of crude oil from the Madison limestone, Beaver Lodge field, in North Dakota. This was the first oil discovered in

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78/ McKinney, C. M., and Garton, E. L., Analyses of Crude Oils From Oklahoma Fields: Petrol. Eng., vol. 25, No. 13, December 1953, pp. A-50--A-53.

79/ Wenger, W. J., and Lanum, W. J., Wyoming and Montana: Characteristics of Crude Oils From Big Horn Basin Fields: Petrol. Eng., vol. 26, No. 2, February 1954, pp. A-52, A-55--A-60.

80/ Wenger, W. J., and Lanum, W. M., North Dakota and Montana: Characteristics of Petroleum From Williston Basin Fields: Petrol. Eng., vol. 26, No. 7, July 1954, pp. C-43, C-45--C-47.

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North Dakota. Tabulated summaries of data showing sources, general characteristics, and analytical and computed information on samples of 20 other crude oils from fields in the Williston Basin in Montana and North Dakota are included.

The article has a map of the area and correlation index curves for Williston Basin crude oils compared with similar curves of typical paraffinic, intermediate, and naphthenic crude oils from other fields.

North Dakota and Montana

The Appendix to Bureau of Mines Report of Investigations 5055[81/] comprises complete Bureau of Mines routine analyses of 22 samples of crude petroleum from fields in North Dakota and Montana. Pertinent information obtained in analyzing the oils is summarized.

Colorado

Petroleum has been produced in Colorado since 1863, but only recently has the State become a major oil producer. The first well was drilled on Oil Creek near Florence, but output in the State was small until discovery and development of the Weber sandstone in the Rangely field. Oil was discovered in the Weber sandstone in 1933, and the reservoir was developed after 1940, bringing Colorado, in 1949, to 11th place among the 48 States as an oil producer. Output increased further in Colorado because of discovery of many fields in the Julesburg basin since 1949. By 1954 Colorado was in 9th place and maintained that position through 1955.

A report[82/] gives analyses of 92 crude oils from 73 fields representing 90 percent of the production in 1955. The samples were analyzed by the Bureau of Mines routine method,[83/] and the results are listed and correlated with geological data. In addition to the routine analyses, nitrogen contents are reported for nearly all the oils.

Most Colorado petroleum samples studied ranged from paraffinic to intermediate, but a few were naphthenic. A large number were high-quality, low-sulfur, green oils; however, the Rangely field, representing the largest single source of production, produces a high-sulfur oil.

The report gives a brief historical background, presents analytical data, correlates analytical data with geological data, and discusses the data in terms of utilization.

81/ Lindsey, K. B., Petroleum in the Williston Basin, including Parts of Montana, North and South Dakota, and Canada, as of July 1953: Bureau of Mines Rept. of Investigations 5055, 1955, 70 pp.

82/ Wenger, W. J., Whisman, M. L., Lanum, W. J., and Ball, J. S., Characteristics and Analyses of Ninety-Two Colorado Crude Oils: Bureau of Mines Rept. of Investigations 5309, 1957, 60 pp.

83/ Work cited in footnote 75, p. 40.

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California

In continuation of the series of analyses of crude oils from fields in California by the Bureau of Mines, a report[84/] presents analyses of 88 samples from 60 fields. In addition to detailed analyses of the samples, data are tabulated on: (1) Production of crude oil during 1953 and through 1953 for some California oilfields, and (2) general information and analytical data on the 88 samples. A list of publications containing analyses of California crude oils by the Bureau of Mines is given in the Appendix.

Asphalts From Rocky Mountain Crude Oils

Some of the asphalts from Rocky Mountain crude oil and other sources are discussed in a paper,[85/] which summarizes work done at the Petroleum Research Center, Laramie, Wyo., from 1935 to June 30, 1954, when the work was discontinued. A total of 117 asphalts were prepared to obtain a series of asphalts of different consistency from each crude oil. Drawings of the apparatus are included in the paper, and the data are presented in seven figures and four tables. A bibliography of 21 references to the literature is appended.

Metal Content of Crude Petroleum

Ball and his coworkers point out[86/] that varied information has been published concerning the metal content of petroleums, but evidently few data are available on the metal content of closely defined crude oils. For this investigation 23 samples of petroleum were collected and analyzed by the Federal Geological Survey for vanadium, nickel, copper, and uranium. Metal content and other properties of the 23 samples of crude petroleum are listed in a table, and a second table correlates data on carbon residue, nitrogen, and sulfur and gives the ratios of vanadium to nickel in the ashes of the oils.

Messrs. Hyden, Horr, and Myers are on the staff of the Geological Survey, U. S. Department of the Interior, at Denver, Colo.

Organic Sulfur Compounds

A brief treatise[87/] on organic sulfur compounds describes the nomenclature and structure of the various classes of organic sulfur compounds

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84/ Garton, E. L., and McKinney, C. M., Analyses of Crude Oils From Some California Fields: Bureau of Mines Rept. of Investigations 5249, 1956, 53 pp.

85/ Stanfield, K. E., Asphalts From Rocky Mountain Crude Oil: Tech. Pub. 21-54, Western Petroleum Refiners Association, Tulsa 3, Okla., Sept. 23-24, 1954, 8 pp.

86/ Ball, J. S., Wenger, W. J., Hyden, H. J., Horr, C. A., and Myers, A. T., Metal Content of Crude Petroleums: Am. Chem. Soc., Div. of Petrol. Chem., Gen. Papers 1, No. 1, 1956, pp. 241-246.

87/ Ball, J. S., Sulfur Compounds, Organic: Encyclopedia of Chem. Technol., vol. 13, 1954, pp. 430-445.

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and their occurrence in biological processes and in petroleum and gives a summary of their reactions, uses, and classes.

Tar Sands

G. B. Shea of the San Francisco Petroleum Research Center of the Bureau of Mines collaborated with K. A. Clark of the Research Council of Alberta, Canada, by preparing the section on U. S. Deposits for an article on Tar Sands in the Encyclopedia of Chemical Technology.[88/] The article deals mainly with the Athabasca oil sands in the Province of Alberta, Canada. The section on U.S. deposits gives a brief description of the principal outcropping deposits of oil-soaked sands in the United States from the viewpoint of their possible use as sources of liquid fuels by separation of the oil from the mineral aggregate.

Synthesis, Properties, and Identification of Sulfur Compounds in Petroleum

American Petroleum Institute

Research Project 48

The formidable problem caused by the presence of sulfur compounds in petroleum, intensified by the increasing rate of production of crude oils of high sulfur content, led to formation in 1948 of American Petroleum Institute (API) Research Project 48. The objectives of this project are the identification and measurement of sulfur compounds in petroleum and the obtaining of fundamental information concerning the physical properties, thermodynamic properties, and other characteristics of synthesized sulfur compounds.[89/] The 1952 report outlined the problems, related the history and organization of the project, and described the accomplishments to the time of the report. Many data on sulfur compounds are given as well as references to publications.

Research Project 48a

The report points out that API Research Project 48 is divided into four phases. Project 48a, The Production, Isolation and Purification of Sulfur Compounds and Measurement of Their Properties, deals with (1) the production and purification of sulfur compounds, conducted at the Laramie Petroleum Research Center at Laramie, Wyo.; (2) measurement of thermodynamic properties, conducted at the Bureau of Mines Petroleum Experiment Station, Bartlesville, Okla.; and (3) identification and measurement of sulfur compounds in crude oils, conducted at the Bartlesville station.

88/ Clark, K. A., and Shea, G. B., Tar Sands: Encyclopedia of Chem. Technol., vol. 13, 1954, ed., pp. 633-645.

89/ Ball, J. S., Bordwell, F. G., Smith, H. M., Waddington, G., and Seyfried, W. D., Synthesis, Properties, and Identification of Sulfur Compounds in Petroleum--a report on API Research Project 48: Proc. API, Sec. I-General Session, Forum on Fundamental Research, vol. 32, (I), November 1952, pp. 139-175.

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Research Project 48b

The fourth phase of API Project 48, which deals with development of methods of synthesis and studies of reactions of sulfur compounds, is conducted at Northwestern University.

Summary for Fiscal Year 1954

In 1954 a second report on API Research Project 48 was presented[90/] at the Annual Meeting of the American Petroleum Institute, Chicago, Ill., November 8 to 11, 1954, as a panel discussion by all five authors. The report points out that excellent progress had been made during the 2 years since publication of the first report in achieving the objectives of obtaining data on sulfur compounds found in petroleum and in identifying individual and type sulfur compounds in a typical (Wasson, Tex.) high-sulfur crude oil. Since 1952, 10 high-purity (99.9+ percent) sulfur compounds had been prepared in large volume, and 35 additional compounds had been obtained in smaller volume. Since 1952 the project had identified 27 sulfur compounds in Wasson crude oil, bringing the total to 43. The boiling range of distillates studied had been increased to 220° C.

The report discusses the various phases of API Project 48, particularly API Project 48a. The discussion is divided into four portions--part I, development of methods of synthesis and studies of the reactions of sulfur compounds; part II, synthesis, purification and property determination; part III, thermodynamic properties of sulfur compounds; and part IV, separation and identification of sulfur compounds.

Synthesis, Purification, and Properties of Organic Sulfur Compounds

Thiols, sulfides, disulfides, and thiophenes of high purity were prepared in the Laramie Laboratory, so that three groups of physical properties could be determined accurately: (1) Common physical properties, including refractive index, density, viscosity, surface tension, melting point, cryoscopic constant, and boiling point; (2) reference spectra, and (3) thermodynamic properties. Properties of the first series of 10 compounds were published in 1954.[91/]

Figure 7 shows the apparatus used at the Laramie Petroleum Research Center for handling and bottling pure organic sulfur compounds.

90/ Ball, J. S., Bordwell, F. G., Smith, H. M., Waddington, G., and Seyfried, W. D., API Research Project 48--Synthesis, Properties, and Identification of Sulfur Compounds in Petroleum: Proc. API, Interdivisional, vol. 34 (VI), 1954, pp. 106-147.

91/ Haines, William E., Helm, R. Vernon, Bailey, C. W., and Ball, J. S., Purification and Properties of Ten Organic Sulfur Compounds: Jour. Phys. Chem., vol. 58, No. 3, March 1954, pp. 270-278.

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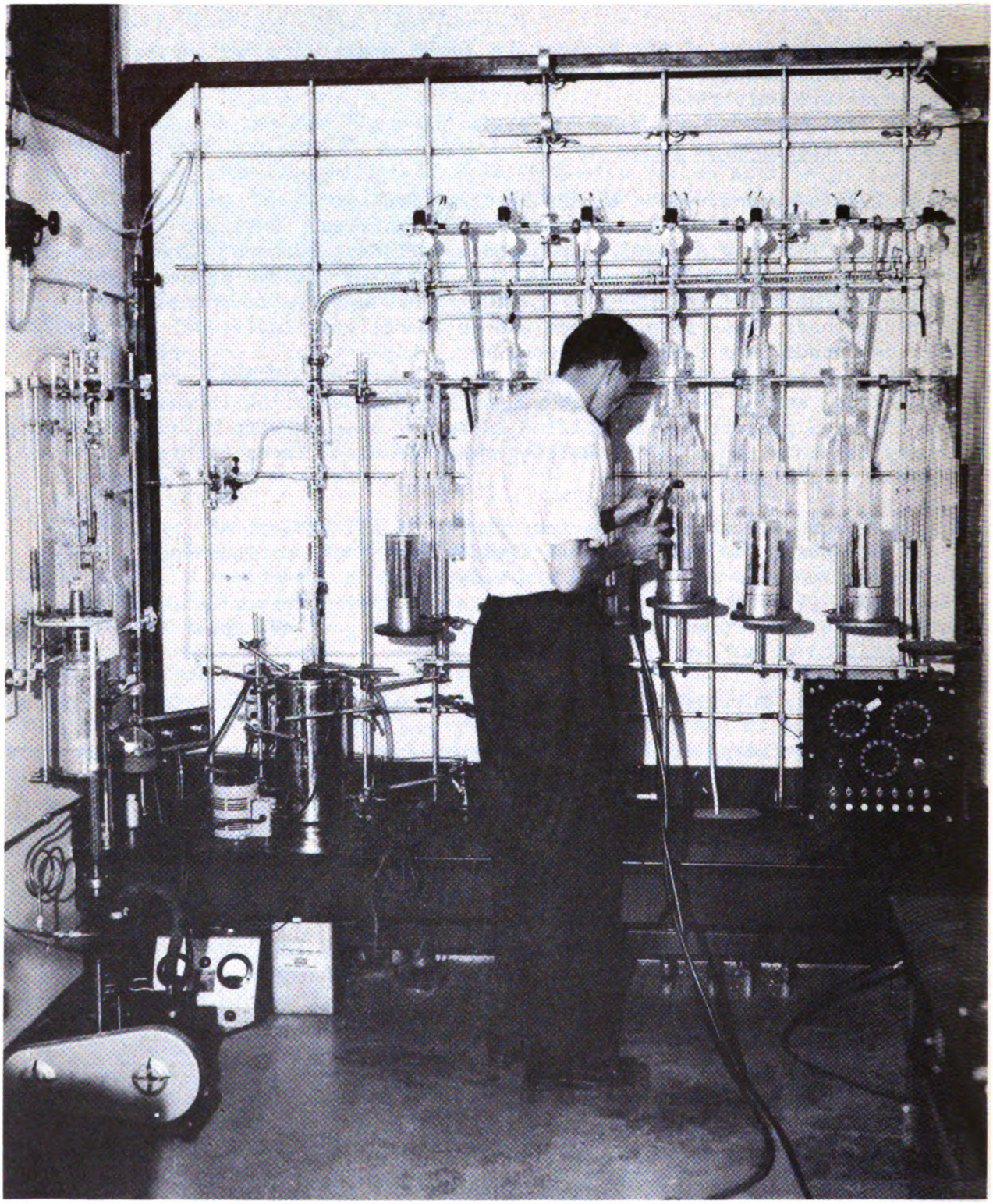

FIGURE 7. - Apparatus Used for Handling and Bottling Pure Organic Sulfur Compounds.

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Literature surveys[92] had shown that data on the physical properties of the thiols, disulfides, and thiophenes were meager. Many of the data available were unreliable because thay had been determined on samples of doubtful purity. Because these types of compounds occur in petroleum products, the production of sulfur compounds in high purity and the accurate determination of their physical properties was undertaken.

The paper describes purification procedures and methods used to determine the stability of the compounds to sunlight. Experimental procedures to determine physical properties are described, and the data are assembled in five tables and four diagrams of spectra.

The second paper in the series[93] reports the common physical properties and spectra of the second series of 10 sulfur compounds. Thermodynamic properties of some of these compounds have been reported in separate publications mentioned elsewhere in this report.[94]

A large enough quantity of each compound was prepared to facilitate the attainment of high-purity (at least 99.9-mole-percent purity) and to assure an adequate supply for measuring properties. A small surplus of each compound usually results; this material is made available to industry as calibration standards through the API Samples and Data Office at Carnegie Institute of Technology, Pittsburgh 13, Pa. Because of their use as calibration standards, the storage stabilities of the compounds have been investigated.

The article lists the 10 sulfur compounds in the second series and describes the methods used for purification. Tables of refractive indices, physical properties, derived functions, mass spectra, and ultraviolet absorption for each of the 10 sulfur compounds are given.

Action of Light on Organic Sulfur Compounds

The action of light on highly purified organic sulfur compounds prepared by API Research Project 48 was investigated as part of a study of the stability of these compounds.[95] The compounds, which are used for instrument

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92/ Haines, W. E., Wenger, W. J., Helm, R. V., and Ball, J. S., Sulfur in Petroleum. II. Boiling Points, Freezing Points, Densities, and Refractive Indices of Some Sulfur Compounds: Bureau of Mines Rept. of Investigations 4060, 1946, 42 pp.
Helm, R. V., Haines, W. E., and Ball, J. S., Sulfur in Petroleum. III. Selected Physical Properties of Some Sulfur Compounds: Bureau of Mines Rept. of Investigations 4566, 1949, 44 pp.

93/ Haines, W. E., Helm, R. V., Cook, G. L., and Ball, J. S., Purification and Properties of Ten Organic Sulfur Compounds--Second Series: Jour. Phys. Chem., vol. 60, No. 5, May 1956, pp. 549-555.

94/ Work cited in footnotes 14 (p. 55), 15 (p. 57), 17 (p. 57), 18 (p. 58), 19 (p. 58), and 21 (p. 59).

95/ Haines, W. E., Cook, G. L., and Ball, J. S., Gaseous Decomposition Products Formed by the Action of Light on Organic Sulfur Compounds: Jour. Am. Chem. Soc., vol. 78, 1956, pp. 5213-5215.

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calibration and research studies, often are stored for considerable periods before use; hence, it is desirable to obtain information about their stability during storage, both in the dark and in the light. Work previously reported[96/] on 20 of the compounds had shown that no decomposition occurs upon dark storage. Thirty highly purified sulfur compounds were exposed to mercury-vapor light under identical conditions and the gaseous decomposition products analyzed by mass spectrometric methods. The technique developed has particular value when the amount of decomposition is small and the purity of the starting material is great enough so that the impurities may be assumed not to be responsible for the products. Some insight into the mechanism of the reaction may be drawn from the results.

The experiments show that the sulfur compounds studied must be protected from light to maintain high purity. Of the various types of sulfur compounds, the thiols were shown to be the most unstable toward light, although all of the compounds showed some instability. The products of decomposition caused by light were different than those obtained from thermal decomposition.

Quantitative Determination of Organic Disulfides

As few published methods for determination of disulfides in petroleum and its products had been tested on a variety of distillates and as disulfides of known purity were available at the Laramie Station, three typical chemical methods were compared; none was suitable for all types of disulfides.[97/] The acid-reflux method gave the best overall recoveries but poor recoveries of disulfides of lower molecular weight. Because of its rapidity, an acid-stirring method was recommended for routine work where tertiary compounds are not a factor. Polarography is unsatisfactory for a wide range of disulfides.

The 15 disulfides tested are listed in the paper with results of sulfur determinations on each compound by three methods: Acid-reflux, acid-stirring, and alkali reduction. The polarographic data are presented graphically.

Separation and Identification of Sulfur Compounds in Petroleum

Methods of Separation of Sulfur Compounds From Petroleum

The newer methods of separation of sulfur compounds in petroleum, particularly as applied by API Research Project 48a were reviewed in a paper[98/] in which the physical methods of distillation, adsorption, and thermal diffusion, and chemical methods, which include adduct and complex formation, are described. Thermal diffusion is stressed, and its application to the separation

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96/ Work cited in footnotes 91 (p. 45), and 93 (p. 47).

97/ Hubbard, R. L., Haines, W. E., and Ball, J. S., Quantitative Determination of Organic Disulfides: Anal. Chem., vol. 30, No. 1, January 1958, pp. 91-93.

98/ Thompson, C. J., Coleman, H. J., Rall, H. T., and Smith, H. M., Separation of Sulfur Compounds From Petroleum: Anal. Chem., vol. 27, No. 2, February 1955, pp. 175-185.

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of sulfur compounds and the constituents of crude oil is discussed. API Research Project 48a had identified and semiquantitatively estimated the content of 43 sulfur compounds in distillate boiling to 220° C. from Wasson, Tex., crude oil. These were concentrated from the crude oil by one or more of the methods discussed in the report, and their semiquantitative identification was established by infrared adsorption spectra or mass spectroscopy.

An all-glass isothermal still was developed to meet the thermal and contact time restrictions that were necessary in processing the crude oil. The stripping unit is operated at atmospheric pressure and at 100° C., with feed rates of approximately 2 liters of crude oil per hour.

The distillate obtained from the isothermal still is fractionated further, and additional separation is accomplished by adsorption.

Sulfur-compound types throughout the complete boiling range of a crude oil, as developed by adsorption and mass spectral data, are given. The names of the 43 compounds and their boiling points, their weight-percent in the Wasson crude oil, and the weight-percent of total sulfur in the crude oil represented by each compound are stated.

The paper contains 8 tables of data and 12 graphs, as well as 13 references to the literature.

Identification of Sulfur Compounds in Petroleum

One of the major parts of the work of API Project 48a is to identify and quantitatively determine the sulfur compounds in a crude oil. The methods developed and applied at the Bartlesville Station to the study of a straight run distillate boiling to 100° C., prepared from Wasson, Tex., crude oil, have been described by Coleman and his coworkers.99/

In essence the problem was to concentrate, without appreciable loss, the sulfur compounds (approximately 40 grams) from 9,000 grams of distillate, to identify these sulfur compounds, and to estimate the concentration in which each is present. Grade H-41 alumina was chosen as the "heart" of the separation process. The various steps used in the separation process are discussed, and the several procedures used to concentrate and separate the sulfur compounds are shown schematically. Fifteen sulfur compounds and elemental sulfur, which were identified in the distillate, are listed in a table. Several of these compounds had not been reported previously as being present in crude oil, so far as the authors could ascertain.

99/ Coleman, H. J., Adams, N. G., Eccleston, B. H., Hopkins, R. L., Mikkelson, Louis, Rall, H. T., Richardson, Dorothy, Thompson, C. J., and Smith, H. M., Analytical Separation and Identification of Sulfur Compounds in a Petroleum Distillate Boiling to 100° C.: Anal. Chem., vol. 28, 1956, pp. 1380-1384.

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Extraction of Thiols

The general procedure for separating sulfur compounds from a distillate that has a boiling range below 100° C. is not satisfactory for distillates of higher boiling range because the number of compounds present becomes so large that it is necessary to devise methods of further separating the mixture into types, each of which may then be distilled and studied. A method that had been developed for separating and recovering thiols[1/] (mercaptans) was used successfully in the separation of thiols from a distillate boiling between 111° and 150° C. The procedure seemed to be limited to thiols containing 16 or fewer carbon atoms. For all practical purposes the procedure is quantitative.

Separation of Thiols

The problems of identifying the sulfur compounds present in petroleum distillates become more complex as the boiling range of the distillate increases. Below 111° C. the sulfur compounds can be identified and quantitatively estimated after concentration by adsorption and distillation.[2/] A method for separating a thiol extract in the C_6--C_{12} range into two groups, one group containing the primary and secondary alkane (and cycloalkane thiols) and the other containing the tertiary alkanethiols, was developed at the Bartlesville Station.[3/] Compounds of the first group form insoluble ammonium mercaptides in liquid ammonia, whereas those of the second group do not. Separation efficiencies ranged from 60 to 98 percent, depending upon the molecular weight and structure of the carbon chain. 5-ethyl-2-nonanethiol could not be separated under the general conditions chosen for the method. The paper gives data showing the application of the method to 10 thiol mixtures.

Identification of Thiophene and 2-Methyl Thiophene

The experimental procedure described in the paper by Thompson and others[4/] was used to prepare a fraction boiling from 38° to 111° C. from Wilmington, Calif., crude oil for identification of thiophene.[5/] This fraction constituted 2.4 percent of the crude oil. To concentrate the sulfur compounds in this fraction, it was percolated batchwise through spray-dried, activated, H-41 (Alcoa) alumina. To increase further the concentration of the sulfur in the sample, 5 ml. was separated in an all-glass concentric-tube column into 15 fractions. Thiophene was found in the 38° to 111° C. boiling-range distillate from Wilmington, Calif., crude oil in a concentration of no less than

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1/ Hopkins, Ralph, and Smith, H. M., Extraction and Recovery of Thiols From Petroleum Distillates: Anal. Chem., vol. 26, No. 1, January 1954, pp. 206-207.

2/ Work cited in footnote 98 (p. 48).

3/ Hopkins, R. L., and Smith, H. M., Separation of Primary and Secondary Thiols From Tertiary Thiols in Liquid Ammonia: Anal. Chem., vol. 27, No. 11, November 1955, pp. 1832-1833.

4/ Work cited in footnote 98 (p. 48).

5/ Thompson, C. J., Coleman, H. J., Mikkelsen, Louis, Yee, Don, Ward, C. C., and Rall, H. T., Identification of Thiophene and 2-Methyl-thiophene in Virgin Petroleum: Anal. Chem., vol. 28, No. 9, September 1956, pp. 1384-1387.

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0.000032 percent. In addition, 2-methylthiopene was identified in the same distillate, and its concentration in the crude oil was estimated at 0.00010 percent. The presence of 3-methylthiophene in the crude oil is probable, but this could not be established with certainty.

Small-Fraction-Receiver

An all-glass receiver was developed to collect a series of small fractions during laboratory distillations and to avoid or minimize a number of undesirable features common to many other types of collection systems.6/ In operation, the distillate falls directly from the tip of the takeoff arm shown in figure 8 of the column into the final receiver. This eliminates the need for stopcocks, thereby avoiding possible contamination of the sample with the stopcock lubricant.

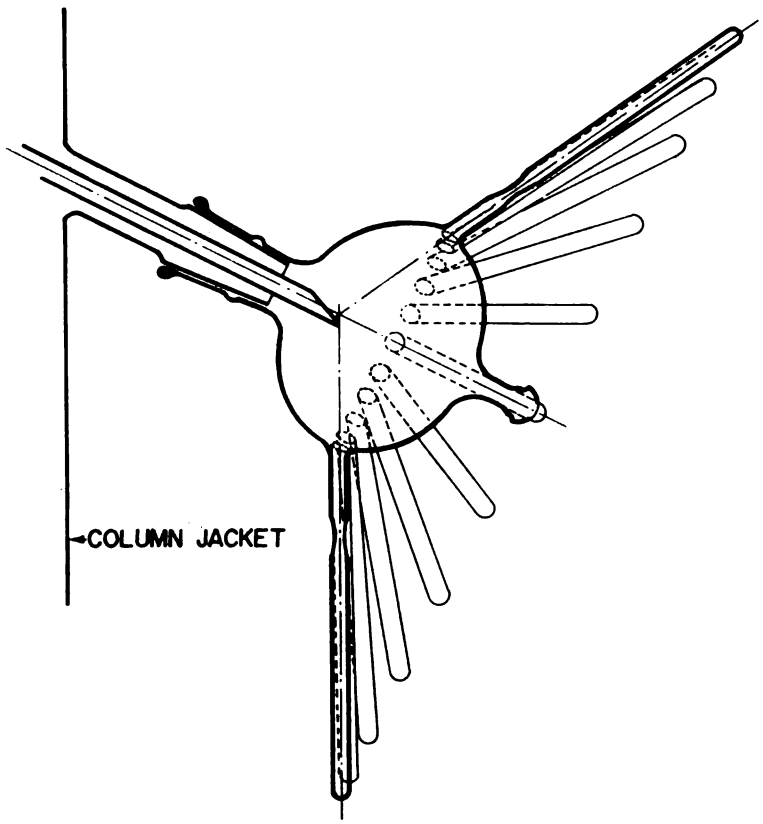

FIGURE 8. - Receiver for Distillation Fractions.

Another advantage of the receiver is that in semimicro distillations the distillate falls directly into the alined receiving tube, thus minimizing sample mixing and holdup. After the desired amount of product has been collected in the collection tube, the device can be rotated on the standard tapered joint to aline a new tube, and the previous fraction is then sealed off. This eliminates evaporation or interchange of vapors between fractions and makes available for immediate use the fraction removed, which is often desirable during extended distillations.

The chilling of the receiver tube directly below the column takeoff arm with dry ice and maintaining the other tubes at room temperature or slightly higher will permit handling low-boiling liquids. The receiver works equally well at atmospheric and reduced pressures. It is particularly advantageous at reduced pressure in that pressure surges and fluctuations in ebullition, which often accompany the changing of receivers during vacuum distillations, are eliminated.

6/ Thompson, C. J., and Coleman, H. J., Unique Unit Handles Micro-Fractions: Petrol. Processing, vol. 9, No. 11, November 1954, pp. 1764-1765.

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The technique avoids ingress of air and moisture and produces a fraction sealed in glass. A collection system as described has been used with good results at the Bureau of Mines laboratory for atmospheric and vacuum distillation and with materials boiling as low as 50° C. A line drawing of the apparatus accompanies the article.

Total Sulfur Content of Hydrocarbons

A rapid and nondestructive method of determining total sulfur on small samples of sulfur compounds was needed in the separation and identification of sulfur compounds in petroleum. X-ray absorption methods met these requirements very well. By modifying existing equipment a method was developed that makes calibration simple and rapid.7/ Monochromatic radiation is obtained by using the fluorescence attachment to an X-ray spectrograph. Samples can be analyzed in about 20 minutes with precision comparable with other X-ray methods and some chemical methods. The procedure is based on the law of absorption of monochromatic electromagnetic energy passing through a homogeneous absorber.

The apparatus and procedure are described and illustrated. The article points out that the equipment used, although perhaps too expensive to warrant its purchase for this purpose alone, is easily and economically adaptable to this problem for laboratories that may have the same or comparable equipment available for other work.

A table lists the results of sulfur determination on 32 distillate fuels, which were analyzed by three methods--bomb, quartz-combustion tube, and the X-ray method described. The standard deviations, which are tabulated, indicate that the X-ray results differ from the bomb results in the same general magnitude as the bomb deviates from theoretical values.

Nitrogen Constituents of Petroleum

American Petroleum Institute Research Project 52

With increasing demand for petroleum products, it became necessary to cut more deeply into crude oils for coking stocks and to utilize crude oils of lower quality; this resulted in stocks with a correspondingly higher nitrogen content. The presence of nitrogen compounds, even in minute quantities, in petroleum fractions has adverse effects on their processing characteristics and the stability of the fuels resulting. Nitrogen compounds "poison" cracking catalysts in gasoline manufacture, resulting in decreased yield of product and shorter catalyst life. These compounds have been shown to cause formation of gums and sludges in distillate fuel oils, as well as "varnish" deposits from gasolines.

The problems posed by nitrogen compounds in the refining of petroleum led to establishment of API Research Project 52--Nitrogen Constituents of

7/ Eccleston, Barton H., and Whisman, Marvin L., Total Sulfur in Hydrocarbons by Monochromatic X-Ray Absorption: Anal. Chem., vol. 28, No. 4, April 1956, pp. 454-458.

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Petroleum.[8] The work on this project has been conducted at three locations: The University of Kansas, Lawrence, Kans., and the Bureau of Mines petroleum stations at Laramie, Wyo., and Bartlesville, Okla. The project was activated July 1, 1954.

A study of the fundamental chemistry of nitrogen compounds, especially from the standpoint of developing separation processes, which may be used to isolate individual compounds or groups of compounds, was assigned to project 52a at the University of Kansas under the supervision of C. A. VanderWerf. Further work assigned to this section includes the development of methods of synthesis for nitrogen compounds.

Separation and identification of nitrogen compounds from crude oil and the preparation of calibration standards for industry were assigned to project 52b at the Bureau of Mines Petroleum Research Center, Laramie, Wyo., under the supervision of John S. Ball. The project was activated July 1, 1954.

Measurements of the thermodynamic properties of the pure nitrogen compounds were to be made by project 52c at the Bureau of Mines Petroleum Experiment Station, Bartlesville, Okla., under the supervision of Guy Waddington.

The article by Ball and others[9] describes the problems caused by the presence of nitrogen compounds in petroleum and outlines the plans for attacking the various aspects of the problem. It includes a list of 25 references to the literature on nitrogen compounds in petroleum, and appendix II lists the papers published by API project 20 and subsequent papers by the University of Texas group.

American Petroleum Institute Research Project 52b (Laramie, Wyo.)

Distribution of Nitrogen Compounds in Wilmington, Calif., Petroleum

The experimental procedures used at Laramie to prepare a concentrate of nitrogen compounds from Wilmington, Calif., petroleum are described in a paper,[10] which also lists the distribution of nitrogen in the crude oil as a function of molecular weight, divides this nitrogen into basic and nonbasic categories and points out some of the precautions necessary to prevent changes in the nitrogen compounds during processing.

Solvent extraction of the crude oil with 15 volumes of normal pentane gave two fractions--the asphaltenes and the deasphaltened oil. The deasphaltened oil contained three-fourths of the nitrogen and was the most convenient and practical for use in identification work because it contained the

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8/ Ball, J. S., VanderWerf, C. A., Waddington, G., and Lake, G. R., API Research Project 52--Nitrogen Constituents in Petroleum: Proc. API, vol. 34, 1954, sec. VI-Interdivisional, pp. 152-165.

9/ Work cited in footnote 8.

10/ Helm, R. V., Latham, D. R., Ferrin, C. R., and Ball, J. S., Distribution of Nitrogen Compounds in Wilmington, Calif., Petroleum: Chem. Eng. Data Series, vol. 2, No. 1, August 1957, pp. 95-100.

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lowest boiling fractions of the crude oil. The asphaltenes, which have the highest molecular weights, comprise approximately one-fifteenth of the oil and contained about one-fourth of the nitrogen. The asphaltene material was of such complexity that detailed study of it was postponed.

A concentrate of the nitrogen compounds was prepared from the deasphaltened oil, using Florisil. Further concentration and separation is planned to identify types of compounds and some individual compounds.

Nitromethane

Because of the importance of nitromethane as an industrial chemical and because of its importance in theoretical considerations as the simplest member of the nitro-paraffin family, many investigations have been made of its physical and chemical properties. In order to make available high-purity nitromethane for thermodynamic measurements, a commercially prepared sample was purified by chemical and physical means to better than 99.9 mole percent as determined by the freezing point method. A paper[11/] describes the purification procedures and presents values for freezing point, density, refractive index, viscosity, and surface tension.

Thermodynamics of Petroleum

Thermodynamics is defined as the science that treats of the mechanical action or relations of heat. The Branch of Thermodynamics at the Bureau of Mines Petroleum Experiment Station, Bartlesville, Okla., uses the principles of this classic science to achieve a twofold objective: (1) To provide accurate values of the chemical thermodynamic properties of petroleum compounds, petrochemicals, and other substances of economic importance; and (2) to extend knowledge of the structure and energetics of matter both as a contribution to fundamental science and as an aid in accomplishing the first objective. These objectives illustrate, respectively, both the concrete and the abstract utility of thermodynamic concepts. In no other laboratory in the world is as complete an ensemble of experimental and theoretical techniques brought to bear in such a systematic fashion upon thermodynamic problems.

The major areas in which research on thermodynamics was conducted in fiscal years 1954, 1955, and 1956 are: (1) Sulfur compounds (API Research Project 48a); (2) nitrogen compounds (API Research Project 52c); (3) fluorine compounds, under contract with the Air Force Office of Scientific Research; (4) hydrocarbons, supported entirely by Bureau of Mines funds; and (5) miscellaneous petroleum derivatives.

11/ Thompson, C. J., Coleman, H. J., and Helm, R. V., The Purification and Some Physical Properties of Nitromethane: Jour. Am. Chem. Soc., vol. 76, No. 13, July 5, 1954, pp. 3445-3446.

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Sulfur Compounds

Heat of Combustion of Sulfur Compounds

Because of the importance of sulfur compounds in petroleum technology and the uncertain factors involved in attempting to determine the heat of combustion of compounds that contain carbon, hydrogen, and sulfur, the Thermodynamics Laboratory of the Bureau of Mines Petroleum Experiment Station, Bartlesville, Okla., developed a rotating bomb method for the determination of the heats of combustion and formation of organic sulfur compounds by bomb calorimetry.12/ A sectional view of the calorimetric system, with the bomb and rotating mechanism in place in the calorimeter, is shown, as well as a top view of the calorimeter system and a perspective view of the calorimeter can. The method is described in detail. Figure 9 shows the rotating combustion bomb in the hands of the operator, and the calorimetric system. The "mirror effect" is caused by reflection from the raised underside of the lid of the constant temperature jacket.

The paper also has a table of data on results of combustion experiments on rhombic sulfur and six sulfur-containing compounds.

Gaseous Sulfur

For full utilization of the thermodynamic data that were being obtained for organic sulfur compounds at the Thermodynamics Laboratory and elsewhere it was necessary to have thermodynamic data of equal quality for elemental sulfur. Data that had become available for elemental sulfur made an up-to-date correlation of some of its thermodynamic properties desirable, and such a correlation was undertaken.13/ Values for the chemical thermodynamic properties of S_8 (gas) were computed from spectroscopic, molecular structure, vapor pressure, and other data as a part of the overall correlation.

2-Propanethiol

Results of detailed studies of the thermodynamic properties of 2-propanethiol, the first of the series of secondary alkane thiols, are presented in a paper14/ that discusses the following closely integrated experimental and

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12/ Hubbard, Ward N., Katz, Charles, and Waddington, G., A Rotating Combustion Bomb for Precision Calorimetry. Heats of Combustion of Some Sulfur-Containing Compounds: Jour. Phys. Chem., vol. 58, No. 2, February 1954, pp. 142-152.

13/ Guthrie, G. B., Jr., Scott, D. W., and Waddington, G., Thermodynamic Functions and Heat of Formation of S_8 (Gas): Jour. Am. Chem. Soc., vol. 76, No. 6, Mar. 20, 1954, pp. 1488-1493.

14/ McCullough, J. P., Finke, H. L., Scott, D. W., Gross, M. E., Messerly, J. F., Pennington, R. E., and Waddington, G., 2-Propanethiol: Experimental Thermodynamic Studies From 12° to 500° K. The Chemical Thermodynamic Properties From 0° to 1,000° K.: Jour. Am. Chem. Soc., vol. 76, No. 19, Oct. 5, 1954, pp. 4796-4802.

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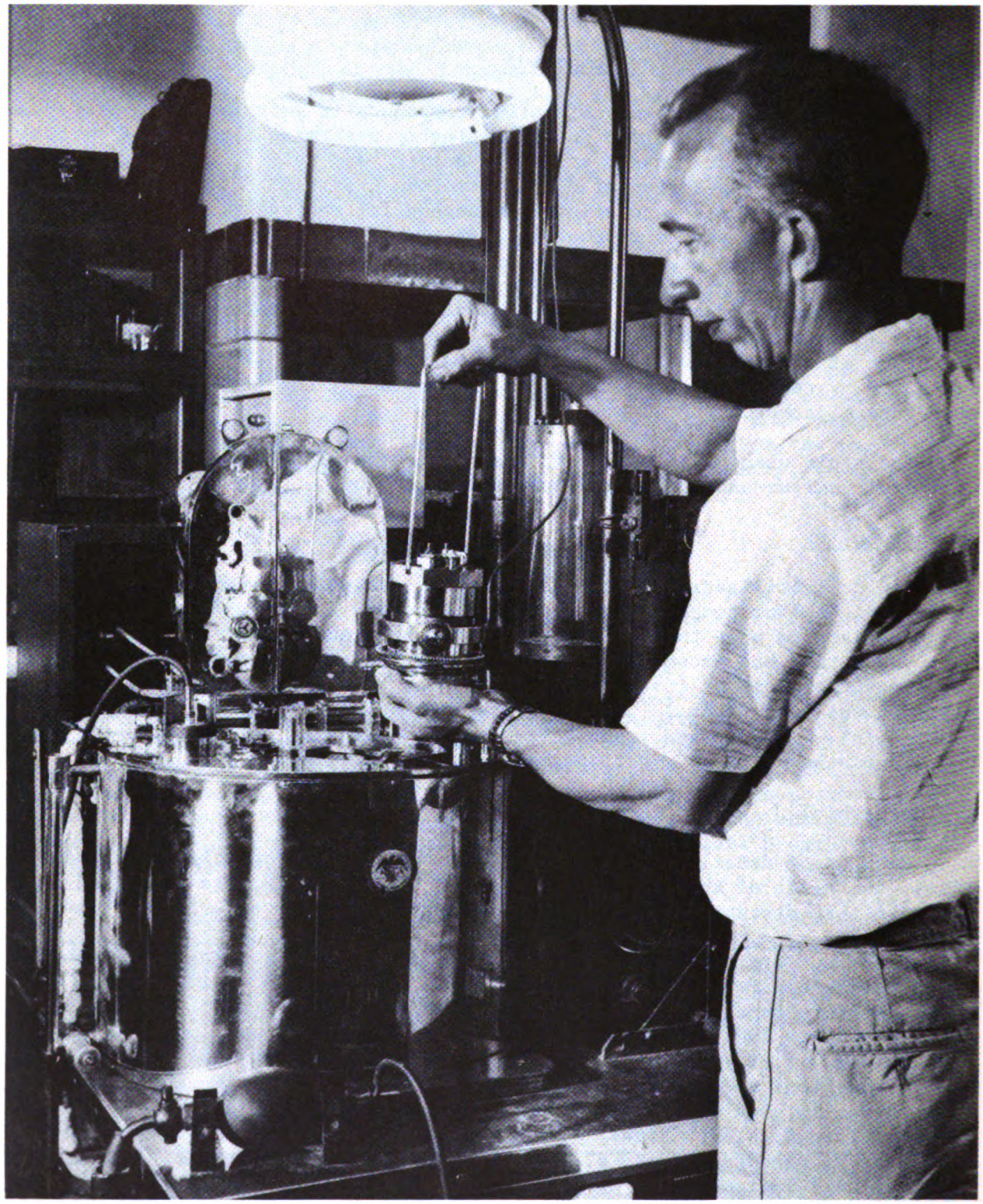

FIGURE 9. - Combustion Calorimetry With Rotating-Bomb Calorimeter, Branch of Thermodynamics, Petroleum Experiment Station, Bartlesville, Okla.

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computational investigations: (1) Low-temperature calorimetric studies, (2) vapor-pressure studies, (3) measurements of the heat of vaporization and vapor heat capacity, (4) determination of the heat of formation, and (5) calculation of thermodynamic functions from spectroscopic, molecular structure, and calorimetric data. The paper has 10 tables of data and a graphical representation of the infrared spectra of 2-propanethiol.

Heats of Combustion, Formation, and Isomerization of 1-Propanethiol, 2-Propanethiol and 2-Thiabutane

A paper (in English) in the journal of the Royal Dutch Chemical Society, The Hague, Holland,15/ gives values of the standard states of formation at 25° C. of each of the three C_3H_8S compounds in the liquid and ideal gaseous states. The reliability of the derived heats of isomerization is discussed.

1-Propanethiol

Results of another study of the class of compounds known as alkanethiols are reported in a paper,16/ which points out that 1-propanethiol is of particular interest because it is the simplest alkanethiol for which rotational tautomerism affects the thermodynamic properties. Detailed investigations of the following thermodynamic properties of 1-propanethiol are discussed in the paper: Calorimetric study of the low-temperature thermal properties in the solid and liquid states; measurement of vapor pressures; investigation of the heat of vaporization and vapor heat capacity; determination of the heat of formation; and calculations of the chemical thermodynamic properties in the ideal gaseous state at selected temperatures from 0° to 1,000° K.

The report includes 12 tables of data on properties of 1-propanethiol.

Ethanethiol and 2-Thiapropane

Ethanethiol and 2-thiapropane are among the important sulfur compounds in the low-boiling fractions of petroleum. The thermodynamic properties of these substances have been the subject of several calorimetric and computational investigations. A paper17/ reports additional calorimetric data that

15/ Hubbard, W. N., and Waddington, G., The Heats of Combustion, Formation, and Isomerization of Propanethiol-1, Propanethiol-2 and 2-Thiabutane: Rec. trav. chim., vol. 73, November 1954, pp. 910-923.

16/ Pennington, R. E., Scott, D. W., Finke, H. L., McCullough, J. P., Messerly, J. F., Hossenlopp, I. A., and Waddington, G., The Chemical Thermodynamic Properties and Rotational Tautomerism of 1-Propanethiol: Jour. Am. Chem. Soc., vol. 78, No. 14, July 20, 1956, pp. 3266-3272.

17/ McCullough, J. P., Hubbard, W. N., Frow, F. R., Hossenlopp, I. A., and Waddington, G., Ethanethiol and 2-Thiapropane: Heats of Formation and Isomerization; the Chemical Thermodynamic Properties From 0° to 1,000° K.: Jour. Am. Chem. Soc., vol. 79, 1957, pp. 561-566.

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permit calculation of the chemical thermodynamic properties of ethanethiol and 2-thiapropane over a wide range of temperatures. The new experimental data include values for the heats of combustion and formation of ethanethiol and 2-thiapropane and for the heat of vaporization and vapor-heat capacity of 2-thiapropane. These data are presented in seven tables.

The samples of ethanethiol and 2-thiapropane were prepared and purified at the Laramie, Wyo., Research Center of the Bureau of Mines.

3-Methyl-2-Thiabutane

Thermodynamic data for 3-methyl-2-thiabutane (methyl isopropyl sulfide), a member of the group of $C_4H_{10}S$ isomers, have been reported.[18] The investigation included experimental studies of 3-methyl-2-thiabutane that provided: (1) Values of the heat capacity in the solid, liquid and vapor states (12° to 500° K.); (2) values of the heats of fusion and vaporization; (3) an equation of state for the vapor, and (4) values of the entropy, S°, heat capacity, C_p°, and heat of formation $\Delta H°$ (gas), in the ideal gaseous state. The calorimetric data were used with spectroscopic and molecular structure data in computing values of thermodynamic properties at selected temperatures from 0° to 1,000° K. The report includes nine tables of data.

Thiacyclohexane

One of the types of sulfur compounds known to occur in crude petroleum and petroleum distillates is the family of cyclic sulfides and their derivatives. Results of thermodynamic investigations of the first three members of the family--thiacyclopropane, thiacyclobutane, and thiacyclopentane--have been presented in publications from the Bartlesville Laboratory. A continuation of the series of papers[19] describes an experimental and computational investigation of the thermodynamic properties of thiacyclohexane. The paper is divided into a section on experimental procedures and a section on calculations of thermodynamic properties.

Thiophene

A note[20] reports the more reliable results obtained with the rotating-bomb method in determining the heat of combustion and heat of formation of

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18/ McCullough, J. P., Finke, H. L., Messerly, J. F., Pennington, R. E., Hossenlopp, I. A., and Waddington, G., 3-Methyl-2-thiabutane: Calorimetric Studies From 12° to 500° K.; the Chemical Thermodynamic Properties From 0° to 1,000° K.: Jour. Am. Chem. Soc., vol. 77, No. 23, Dec. 5, 1955, pp. 6119-6125.

19/ McCullough, J. P., Finke, H. L., Hubbard, W. N., Good, W. D., Pennington, R. E., Messerly, J. F., and Waddington, G., The Chemical Thermodynamic Properties of Thiacyclohexane From 0° to 1,000° K.: Jour. Am. Chem. Soc., vol. 76, No. 10, May 20, 1954, pp. 2661-2669.

20/ Hubbard, W. N., Scott, D. W., Frow, F. R., and Waddington, G., Thiophene: Heat of Combustion and Chemical Thermodynamic Properties: Jour. Am. Chem. Soc., vol. 77, No. 22, Nov. 20, 1955, pp. 5855-5857.

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thiophene, and gives values for the heat and free energy of formation of thiophene as a function of temperature calculated by use of these results. The experimental techniques are described, and three tables of data are given.

2-Methylthiophene

Thiophene derivatives constitute an important fraction of the organic sulfur compounds found in petroleum. To provide the basic information needed for computing thermodynamic data for this class of compounds by approximate and empirical methods, detailed studies were being made of the thermodynamic properties of selected thiophene derivatives. Data for 2-methylthiophene are presented in a paper[21/] that describes studies by the methods of low-temperature calorimetry, flow calorimetry, and combustion calorimetry. The results include values of the heat capacity in the solid, liquid, and vapor states and the heats of fusion, vaporization, and combustion. From these data were obtained values of the entropy, heat capacity, and heat of formation of 2-methylthiophene in the ideal gaseous state. The calorimetric results were used with spectroscopic and molecular structure information to calculate values of thermodynamic functions at selected temperatures from 0° to 1,000° K. Data are presented in 10 tables.

Benzothiophene

A study of the low-temperature thermal properties of benzothiophene[22/] provided values for the following thermal properties of benzothiophene, as determined by the methods of low-temperature calorimetry: The heat capacity of two crystalline modifications and of the liquid (12°-335° K.), and the heats of transition and fusion, the triple point, the cryoscopic constant, and the entropy of the solid at 298.16° K. (25° C.) and of the liquid at the triple point. The difference in entropy of the two crystalline modifications is discussed in terms of a possible order-disorder phenomenon.

Benzenethiol

The thermodynamic properties of benzenethiol (thiophenol) (C_6H_5SH)[23/] were studied as part of the program of the Thermodynamics Laboratory to obtain thermodynamic data for organic sulfur compounds of interest in petroleum

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21/ Pennington, R. E., Finke, H. L., Hubbard, W. N., Messerly, J. F., Frow, F. R., Hossenlopp, I. A., and Waddington, Guy, The Chemical Thermodynamic Properties of 2-Methylthiophene: Jour. Am. Chem. Soc., vol. 78, No. 10, May 20, 1956, pp. 2055-2060.

22/ Finke, H. L., Gross, M. E., Messerly, J. F., and Waddington, G., 2,3 Benzothiophene: Heat Capacity, Heat of Transition, Heat of Fusion and Entropy. An Order-Disorder Transition: Jour. Am. Chem. Soc., vol. 76, No. 2, Feb. 5, 1954, pp. 854-857.

23/ Scott, D. W., McCullough, J. P., Hubbard, W. N., Messerly, J. F., Hossenlopp, I. A., Frow, F. R., and Waddington, G., Benzenethiol: Thermodynamic Properties in the Solid, Liquid, and Vapor States; Internal Rotation of the Thiol Group: Jour. Am. Chem. Soc., vol. 78, No. 21, Nov. 5,1956, pp. 5463-5468.

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technology. The most significant results, values of the entropy, heat capacity, and heat of formation of benzenethiol vapor, are given in table I of the report. Calculations of the thermodynamic properties are discussed in detail. The experimental methods and methods of correlating the data are described.

Nitrogen Compounds

Nitromethane

This compound[24] was studied further in the Thermodynamic Laboratory[25] to provide more accurate and extensive values of its chemical thermodynamic properties. The experimental studies consisted of determinations of: (1) The vapor pressure at 15 temperatures from 55° to 136° K.; (2) the heat of vaporization at four temperatures from 318° to 374° K.; and (3) the vapor heat capacity at two to four pressures at each of six temperatures from 363° to 523° K. The heat capacity in the ideal gas state and an equation of state for the real vapor were obtained from the experimental results. These thermodynamic data, with data from other sources, were used in calculations of the chemical thermodynamic properties of nitromethane at selected temperatures from 0° to 1,500° K.

The experimental apparatus and procedures are described, and the data are given in four tables.

Additional data on nitromethane are given in a brief article[26] which demonstrates the advantage of using the vapor heat capacity and the second virial coefficient for determining the intermolecular potential energy parameters of nitromethane.

Pyridine

From studies of low-temperature calorimetry, comparative ebulliometry, flow calorimetry, and combustion calorimetry, values were obtained for the entropy, heat capacity, and heat of formation of pyridine in the ideal gas state.[27] The calorimetric values of entropy and heat capacity served as guides in revising the vibrational assignments for pyridine and several

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24/ Work cited in footnote 11 (p. 54).

25/ McCullough, J. P., Scott, D. W., Pennington, R. E., Hossenlopp, I. A., and Waddington, Guy, Nitromethane: The Vapor Heat Capacity, Heat of Vaporization, Vapor Pressure and Gas Imperfection; the Chemical Thermodynamic Properties From 0° to 1,500° K.: Jour. Am. Chem. Soc., vol. 76, Oct. 5, 1954, pp. 4791-4796.

26/ Douslin, D. R., and Waddington, Guy, Intermolecular Potential Energy of Dipolar Gases From Heat-Capacity Data: Jour. Phys. Chem., vol. 23, 1955, pp. 2453-2454.

27/ McCullough, J. P., Douslin, D. R., Messerly, J. F., Hossenlopp, I. A., Kincheloe, T. C., and Waddington, Guy, Pyridine: Experimental and Calculated Chemical Thermodynamic Properties Between 0° and 1,500° K.; a Revised Vibrational Assignment: Jour. Am. Chem. Soc., vol. 79, No. 16, Aug. 20, 1957, pp. 4289-4295.

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deuteropyridines. The revised assignment for pyridine and molecular structure data were used in computing values of the thermodynamic functions at selected temperatures between 0° and 1,500° K. Values of the heat, free energy, and equilibrium constant of formation were calculated at the same selected temperatures.

The experiments are described, and the data are reported in 11 tables.

Hydrocarbons

Normal Paraffin Hydrocarbons

Because of the importance of the normal paraffins in petroleum technology, the entropies of the compounds from normal octane to normal hexadecane were redetermined in the Thermodynamics Laboratory at Bartlesville, Okla.[28/] Previously reported values of the entropy of some of these hydrocarbons were based on heat-capacity measurements over a somewhat limited temperature range on compounds of uncertain purity. The materials used in the investigation were API research samples. Their purity is discussed in the paper.

The new measurements resulting from this work provide a more reliable value for the entropy of each compound in the liquid state at 298.16° K. (25° C.), which, when appropriately combined with heat of vaporization and vapor-pressure data, yields a value of the entropy of each compound in the ideal gaseous state.

2,3-Dimethyl-2-Butene

Calorimetric studies on 2,3-dimethyl-2-butene were made as another part of the continuing program of the Thermodynamics Laboratory at Bartlesville, Okla., to measure thermodynamic properties of hydrocarbons important in petroleum technology.[29/]

The 2,3-dimethyl-2-butene used for low-temperature calorimetry and for measurement of vapor pressure was an API research sample made available through the API Research Project 44, Collection, Analysis, and Calculation of Data on Properties of Hydrocarbons. The sample was purified by API Research Project 6, Analysis, Purification, and Properties of Hydrocarbons, from material supplied by the General Motors Corporation, Detroit, Mich.

28/ Finke, H. L., Gross, M. E., Waddington, Guy, and Huffman, H. M., Low-Temperature Thermal Data for the Nine Normal Paraffin Hydrocarbons From Octane to Hexadecane: Jour. Am. Chem. Soc., vol. 76, No. 2, Jan. 20, 1954, pp. 333-341.

29/ Scott, D. W., Finke, H. L., McCullough, J. P., Gross, M. E., Messerly, J. F., Pennington, R. E., and Waddington, Guy, 2,3-Dimethyl-2-butene: Thermodynamic Properties in the Solid, Liquid, and Vapor States: Jour. Am. Chem. Soc., vol. 77, No. 19, Oct. 5, 1955, pp. 4993-4998.

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The experimental procedures and the methods used by the authors for calculating the derived properties are described in the paper, and the thermodynamic data are presented in 10 tables.

Cyclic Hydrocarbons

Results of studies of low-temperature thermal properties of three cyclic hydrocarbons are reported in a paper30/ which shows that, in the solid state, the thermal behavior of each substance is complex; there are transitions between four different crystalline forms of cycloheptane, three of cyclooctane, and two of 1,3,5-cycloheptatriene.

From determinations of low-temperature thermal properties and vapor pressure for each of the three compounds, values of the entropy in the liquid and vapor states and the heat of vaporization, all at 298.16° K., were obtained. These results and values of heats of formation derived from the literature were used to compute values for other properties in the liquid and vapor states at 298.16° K. The report contains 12 tables of data.

Halogen Compounds

Combustion Calorimetry of Organic Chlorine Compounds

A method for determining the heats of combustion of organochlorine compounds in a conventional bomb calorimeter is described in a paper31/ that outlines the problems involved in the determination and describes a modification of the method that had been used previously. Application of the modified method was only partly successful, and other procedures were contemplated.

The problem of determining the heats of combustion of chlorine-containing compounds is that of devising equipment and techniques that will leave a final state in the bomb that is capable of being defined thermodynamically and interpreted thermochemically. It is shown in the paper that experiments have been performed to indicate the magnitude of the thermal effects produced by known uncertainties. The method is shown to give results of good precision, and it will be satisfactory when accuracy requirements are moderate. It has the advantage that combustion equipment of conventional design can be utilized with only slight modifications.

Results of combustion experiments on chlorobenzene, orthochlorobenzene, parachlorobenzene, orthodichlorobenzene, metadichlorobenzene, and paradichlorobenzene are tabulated.

30/ Finke, H. L., Scott, D. W., Gross, M. E., Messerly, J. F., and Waddington, Guy, Cycloheptane, Cyclooctane and 1,3,5-Cycloheptatriene. Low-Temperature Thermal Properties, Vapor Pressure and Derived Chemical Thermodynamic Properties: Jour. Am. Chem. Soc., vol. 78, No. 21, Nov. 5, 1956, pp. 5469-5476.

31/ Hubbard, W. N., Knowlton, J. W., and Huffman, H. M., Combustion Calorimetry of Organic Chlorine Compounds. Heats of Combustion of Chlorobenzene, the Dichlorobenzenes and o- and p- chloroethylbenzene: Jour. Phys. Chem., vol. 58, May 1954, pp. 396-402.

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Combustion Calorimetry of Organic Fluorine Compounds

A new and improved rotating-bomb calorimeter was constructed as a result of an investigation which was undertaken to develop a rotating-bomb method for combustion calorimetry of organic fluorine compounds.[32/] The authors point out that the combustion calorimetry of organic fluorine compounds has received little attention, and no studies of this class of compounds had been made previously by the methods of modern precision combustion-bomb calorimetry.

The calorimeter is similar in most of the essential features to the earlier model.[33/] The most significant change is in the method of rotating the bomb by a direct drive gear, instead of by withdrawal of a spiral wire wound around a pulley, so that the bomb may be rotated as long as desired. Using this apparatus, calorimetric studies were made with six organic fluorine compounds selected to include volatile liquids, nonvolatile solids, a group of isomeric compounds, and compounds with a wide range of fluorine content (14-76 percent). The use of comparison experiments and the special technique for volatile samples are cumbersome and time-consuming procedures, which, however, are necessary if accuracy is to be achieved.

The authors conclude that the results with compounds of different physical state, volatility, and fluorine content show that the rotating-bomb method is satisfactory for accurate combustion calorimetry of most of the solid and liquid organic fluorine compounds.

The research was supported by the U.S. Air Force, through the Office of Scientific Research of the Air Research and Development Command.

Heats of Hydrolysis and Formation of Tetrafluoromethane

As part of a broad program of combustion calorimetry of solid and liquid organic fluorine compounds, the heats of hydrolysis and formation of tetrafluoromethane (CF_4) were determined as a byproduct of combustion calorimetric investigations of tetrafluoroethylene.[34/] The combustion experiments were made with the rotating-bomb calorimeter, using polytetrafluoroethylene with hydrocarbon oil in the presence of water. Errors in the experimental determinations and in reduction of the data to standard states were minimized by comparative experiments in which hydrofluoric acid solution was initially added to the bomb, and the charge was a mixture of benzoic acid and oil or of benzoic acid and succinic acid. The comparative experiments were so designed that the energy evolved and the amounts of final products (except CF_4) were essentially the same in the combustion and comparative experiments.

32/ Good, W. D., Scott, D. W., and Waddington, Guy, Combustion Calorimetry of Organic Fluorine Compounds by a Rotating-Bomb Method: Jour. Phys. Chem., vol. 60, No. 8, August 1956, pp. 1080-1089.

33/ Work cited in footnote 12 (p. 55).

34/ Scott, D. W., Good, W. D., and Waddington, Guy, Heat of Formation of Tetrafluoromethane From Combustion Calorimetry of Polytetrafluoroethylene: Jour. Am. Chem. Soc., vol. 77, No. 1, Jan. 5, 1955, pp. 245-246.

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This research also was supported by the U.S. Air Force, through the Office of Scientific Research of the Air Research and Development Command.

Fluorobenzene

Another report on research that was supported by the U.S. Air Force through the Office of Scientific Research of the Air Research and Development Command[35/] points out that the chemical thermodynamics of organic fluorine compounds have received increasing attention in recent years. The paper reports a comprehensive study of fluorobenzene, the simplest member of the class of aromatic fluorine compounds. Experimental studies were made by the methods of low temperature calorimetry, comparative ebulliometry, flow calorimetry, and combustion calorimetry. Detailed results of these studies are given. The most significant results were values of the entropy, heat capacity, and heat of formation of fluorobenzene vapor. Ten tables of data are included.

Organometallic Compounds

Despite the commercial importance of tetraethyllead as an antiknock agent in motor fuels, no reliable value for its heat of formation was available when the determination was undertaken at the Thermodynamics Laboratory of the Bartlesville Station.[36/] The investigation was part of the continuing program of chemical thermodynamic studies of compounds important in petroleum technology.

The heat of formation of tetraethyllead was determined by combustion calorimetry using the rotating bomb described in the paper by Good and his coworkers.[37/] A solution of nitric acid and arsenious acid was used in the bomb to convert all lead-containing products of combustion to Pb ++ ion.

The investigation demonstrated the applicability of the rotating-bomb method to combustion calorimetry of compounds that normally yield ill-defined combustion products. With this method the solid products can be dissolved to give a well-defined final state of the combustion process. Experimental and analytical data are tabulated and discussed.

The Research Laboratories of the Ethyl Corporation contributed financial support and a sample of purified tetraethyllead to the investigation.

35/ Scott, D. W., McCullough, J. P., Good, W. D., Messerly, J. F., Pennington, R. E., Kincheloe, T. C., Hossenlopp, I. A., Douslin, D. R., and Waddington, Guy, Fluorobenzene: Thermodynamic Properties in the Solid, Liquid and Vapor States: A Revised Vibrational Assignment: Jour. Am. Chem. Soc., vol. 78, No. 21, Nov. 5, 1956, pp. 5459-5463.

36/ Scott, D. W., Good, W. D., and Waddington, Guy, Tetraethyllead: Heat of Formation by Rotating-Bomb Calorimetry: Jour. Phys. Chem., vol. 60, No. 8, August 1956, pp. 1090-1096.

37/ Work cited in footnote 32 (p. 63).

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Reference-Book Publications

Members of the staff of the Thermodynamics Laboratory at Bartlesville, Okla., have contributed chapters to reference books on thermodynamics and related subjects. These chapters are summarized in the following section.

Thermochemistry and the Thermodynamic Properties of Substances

A review of the thermochemistry and the thermodynamic properties of substances[38] points out that this branch of physical chemistry had its beginning in the period when chemistry emerged as a recognized branch of natural philosophy, going back to Antoine Lavoisier, and is at least 170 years old. The review covers recent publications on thermochemistry and chemical thermodynamics that were not covered by previous reviews of the series and that were available to the reviewer in the original or as abstracts before January 1, 1955. The data are discussed and tabulated as: (1) Chemical thermodynamics of inorganic substances, (2) chemical thermodynamics of organic substances, and (3) data of state. A feature that was particularly evident in the survey of present-day chemical thermodynamics was the fundamental importance of careful experimentation and accurate measurement. A list of 178 references is appended.

Experimental Thermochemistry

A book prepared under the auspices of the International Union of Pure and applied Chemistry, Subcommission on Experimental Thermochemistry,[39] includes four chapters by members of the Thermodynamics Laboratory of the Bureau of Mines at Bartlesville, Okla.:

Chapter 5, Standard States. - The purpose of this chapter is to consider the correction to standard states of bomb calorimetric data for sulfur, nitrogen, and halogen compounds, the general formulas of which are $C_aH_bO_cS_d$, $C_aH_bO_cN_d$, $C_aH_bO_cCl_d$, $C_aH_bO_cBr_d$, and $C_aH_bO_cI_d$. The corrections for these classes of compounds include the simpler corrections for compounds of the general formula, $C_aH_bO_c$, as limiting cases when d is zero, and for compounds of the general formula, C_aH_b as limiting cases when both c and d are zero. The corrections may be applied at any temperature between 20° C. and 30° C.

Chapter 7, Combustion of Organic Sulfur Compounds. - Application of the bomb-calorimetric method for determination of the heat of combustion of organic compounds containing sulfur involves many specific difficulties. These difficulties have been alleviated by a new combustion technique using a moving-bomb system. The difficulties introduced into bomb calorimetry when

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38/ Scott, D. W., Thermochemistry and the Thermodynamic Properties of Substances: Annual Review of Physical Chemistry, vol. 6, 1955, pp. 1-24 (Annual Reviews, Inc., Stanford, Calif.).

39/ Rossini, Frederick (ed.), Experimental Thermochemistry--Measurement of Heat of Reaction: Interscience Publishers, Inc., 250 Fifth Avenue, New York 1, N. Y., 1956, 326 plus XV pp.

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sulfur compounds are studied and the means for overcoming these difficulties are summarized.

A description and evaluation of the method are presented with a detailed description of the construction and operation of a typical rotating-bomb calorimeter. A number of factors producing effects of small magnitude are examined, and the conclusion is reached that the heats of combustion of sulfur compounds may be determined with good precision by the moving-bomb method. Further improvements in the method are possible and will materialize if investigations now in progress are continued. For investigators requiring only moderate accuracy, the Huffman-Ellis method is available.

Chapter 8, Combustion of Organic Chlorine Compounds. - The precise determination by bomb-calorimetric methods of the heats of combustion of organic halogen (fluorine, chlorine, bromine, and iodine) compounds is accompanied by problems of the same general nature as those encountered in studies of organic sulfur compounds, but the solution of these problems for organic halogen compounds has been less satisfactory than for organic sulfur compounds.

The historical development of solutions of the problems associated with the determinations of heats of combustion of chlorine is reviewed. Three experimental procedures (two static methods and the moving-bomb method) are described, and the results obtained by each method are compared. The authors conclude that no method for the determination of heats of combustion of chlorine compounds has yet been developed to a point that the accuracy of the results obtainable is comparable to the existing body of thermodynamic data for hydrocarbons. Critical reexamination of the overall chemistry of the combustion process will be required to improve further the methods discussed in the chapter.

Chapter 13, Physicochemical Standards. - This chapter discussed the requirements for accurate determination of the change in internal energy when specific reactants in known thermodynamic states are converted into specific products also in known thermodynamic states. The various experimental devices employed and dissimilar methods for obtaining the same thermochemical quantity necessitate a means of evaluating the number of units of energy involved in the specific thermochemical process that takes place in the calorimetric equipment. Because of the expense involved in electric methods of measuring the temperature increment, most laboratories determine the energy equivalent of a calorimetric system by use of a standard reference substance certified by a standardizing laboratory as to the amount of heat it will produce when a specified mass of the substance is burned in a bomb under prescribed conditions.

The use of benzoic acid as a primary standard for bomb calorimetry is discussed, as well as its advantages over naphthalene and sucrose for this purpose.

The function of secondary standards for bomb combustions of compounds containing nitrogen, sulfur, chlorine, bromine, or iodine differs somewhat from that of the primary standard, benzoic acid, because the products of combustion and conditions of the experiment may differ considerably from those

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common in studies of compounds containing carbon, hydrogen, and oxygen. Requirements for satisfactory test substances for sulfur compounds, halogen compounds, and nitrogen compounds are discussed, and the difference in the function of the primary standard benzoic acid, and of a test substance for a particular problem is emphasized.

Chemical Studies of Liquid Fuels

Aromatics in Jet Fuels

In a report[40/] of studies partly financed by the Air Materiel Command, U.S. Air Force, the composition of the aromatic portion of petroleum distillates in the jet-engine (JP-4)-fuel boiling range was investigated to provide information that may be related to burning characteristics of the distillates. Application of the method was limited to the 420° to 600° F. range because distillate boiling between these temperatures contains most of the polycyclic aromatic hydrocarbons in JP-4 fuel.

A high-dilution alumina-adsorption fractionation provided compositional data and samples to study burning quality by a smoke-lamp test. Smoke points were thus correlated with the presence of different aromatic types. The method was applied to aromatic concentrates prepared from fuels from 11 crude oils, selected to provide fuels with considerable variation in composition. The data are presented in eight figures and three tables.

Storage Stability of Distillate Fuels

Studies of storage stability of distillate fuels, jointly financed by the Western Petroleum Refiners Association and the Bureau of Mines, were begun at the Bureau of Mines Petroleum Experiment Station, Bartlesville, Okla., in May 1951. Subsequently, the Bureau of Ships, Department of Navy, contributed to certain phases of the work. A report on the study[41/] was presented at the National Diesel Engine Meeting, Chicago, Ill., November 3 to 4, 1953. An abstract of the paper and of three comments appears in the SAE Journal.[42/]

40/ McKinney, C. M., and Hopkins, R. L., Alumina-Adsorption Analysis of Petroleum Aromatics in 420° to 600° F. Range: Anal. Cham., vol. 26, No. 9, September 1954, pp. 1460-1465.

41/ Schwartz, F. G., Ward, C. C., and Smith, H. M., Studies on the Storage Stability of Distillate Fuels; Results of Storage Tests: Bureau of Mines, Bartlesville, Okla., SAE No. 189. Available in multilithographed form from the Society of Automotive Engineers, Special Publications Department, 485 Lexington Avenue, New York 17, N. Y.

42/ Why Distillate Fuels Deteriorate in Storage. Abs. based on paper by F. G. Schwartz, C. C. Ward, and H. M. Smith: SAE Jour., February 1954, pp. 107-109.

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A subsequent report[43/] points out that the first objective of the work was to find fuels that are unstable and blends of fuels that are incompatible in storage. The second objective was to study the fundamental causes of instability and incompatibility.

The first objective has been attained, and the data are presented in the report. The data were obtained from storage of 34 fuels and 120 blends at 110° F. in vented bottles and a comparison of bottle and drum storage at ambient temperatures, with storage at 110° in bottles. On the basis of the data presented, a number of conclusions are drawn concerning the relative stability of fuels and blends, effects of variables in blending, and the relative severity of drum and bottle storage.

Compatibility effects encountered in blending are illustrated in tables and graphs, and the data emphasize the extreme difficulty of developing a single correlation of stability with physical or chemical properties that would predict storage stability of all fuels and blends.

Trace Metals

One phase of the Bureau of Mines study of distillate-fuel storage stability required determination of a large number of metals present in trace quantities in these fuels.[44/]

Figure 10 shows a Beckman Model DU flame spectrophotometer, which was modified for this work by installing an automatic wavelength drive (fig. 11), and a recorder, which reduced the time needed for analysis to about 10 minutes and the sample requirements to 10 ml. These modifications are described, and spectrograms of 20 metals are given, with tables of the principal flamelines and an estimated detection limit for each of the metals. The data presented can be used in planning the analysis for any particular metal or combination of metals, as well as aiding the identification of lines in flame spectra. A method of analysis for metals in distillate fuels is outlined briefly.

Constant-Volume Bomb

Since 1948 the Petroleum Experiment Station of the Bureau of Mines at Bartlesville, Okla., has been working on the development and refinement of equipment and techniques for studying the ignition and combustion of liquid fuels in a constant-volume bomb.[45/] This work was done in cooperation with

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43/ Bureau of Mines, Distillate Fuel Storage Stability: 1957, 103 pp. (Pamphlet) Available from Western Petroleum Refiners Association, Tulsa 3, Okla.; Oil Gas Jour., 1957: June 3, p. 121; June 21, p. 176; July 8, p. 144; July 22, p. 111; Aug. 5, p. 98; Oct. 7, p. 177; Oct. 21, p. 139; Dec. 2, p. 116; and Dec. 16, p. 129.

44/ Whisman, M., and Eccleston, B. H., Flame Spectra of Twenty Metals Using a Recording Flame Spectrophotometer: Anal. Chem., vol. 27, No. 12, December 1955, pp. 1861-1869.

45/ Hurn, R. W., and Hughes, K. J., Constant-Volume Combustion of Diesel Fuels: Proc. API Div. of Ref., vol. 30M (III), 1950, pp. 227-237.

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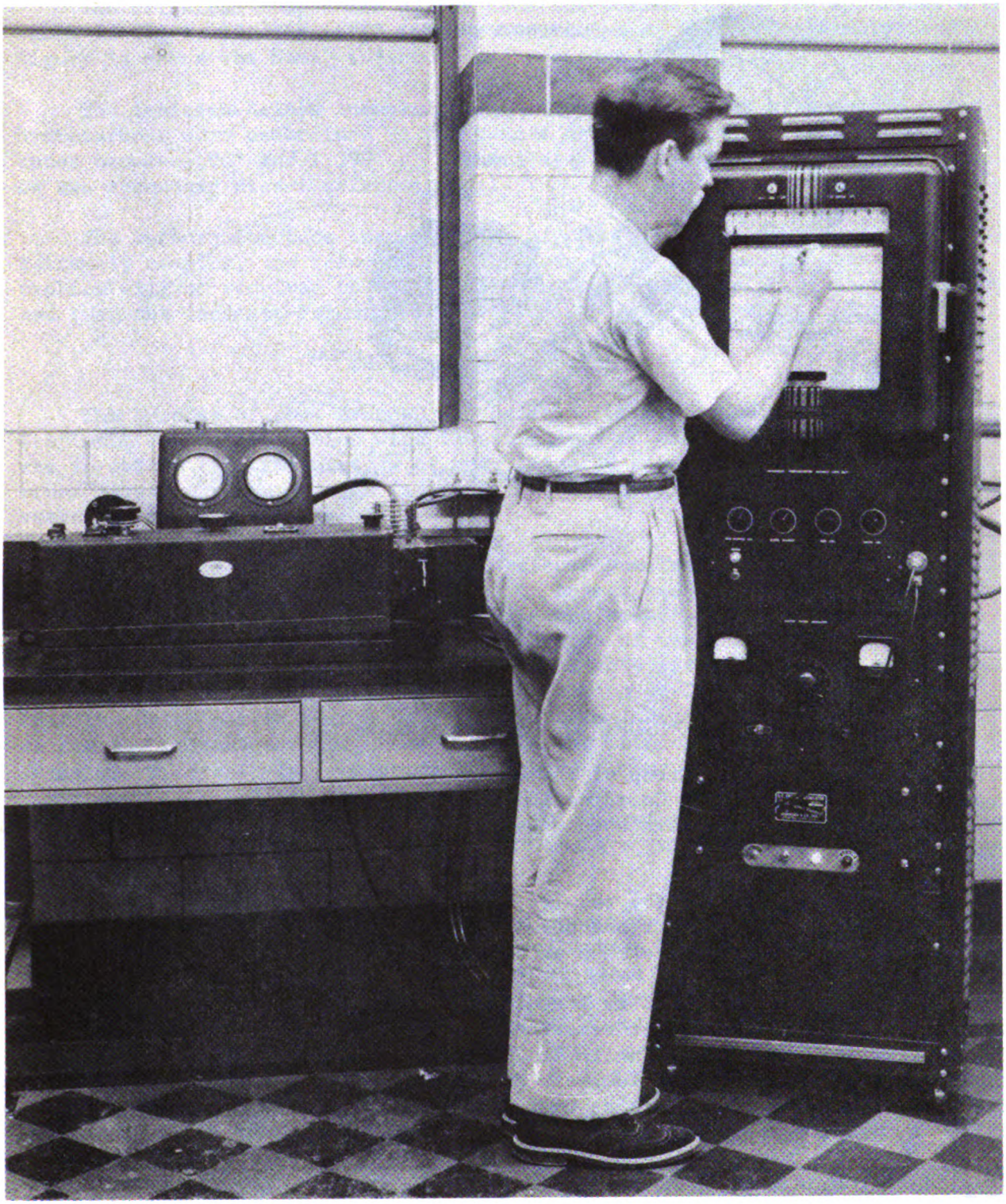

FIGURE 10. - Recorder, Power Supply, and Wave-Length Drive Attached to Beckman DU Flame Spectrophotometer.

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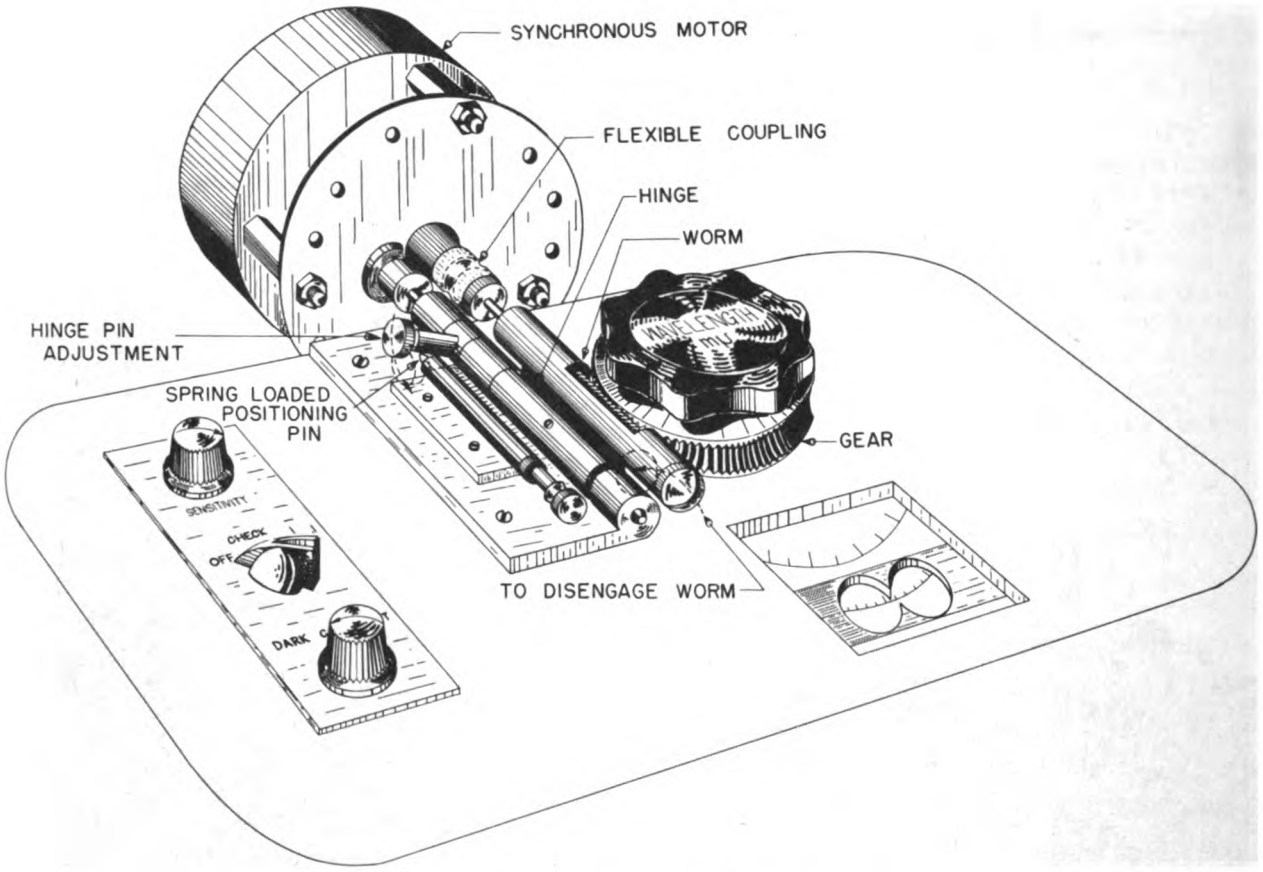

FIGURE 11. - Wavelength Drive.

the Diesel Bomb Advisory Group of the Diesel Fuels Division of the Coordinating Research Council (CRC) Coordinating Fuel and Equipment Research Committee. The results of this work have been presented in a series of CRC progress reports.

A paper[46/] summarizes the results on the effect of operating variables and fuel structure and points out possible applications of a constant-volume bomb to fundamental studies of the autoignition and combustion of fuels.

The constant-volume bomb is a reaction chamber that can be charged with air and maintained at constant temperature. A measured quantity of fuel can be injected into the bomb in a single injection, and the subsequent pressure-time history of the reacting fuel-air mixture in the bomb can be recorded. The unit is designed for tests at bomb temperatures ranging from 400° to 1,500° F. and for tests at initial bomb charging pressures up to 800 p.s.i.g.

46/ Elliot, M. A., Hurn, R. W., and Trimble, H. M., Autoignition of Fuels in a Constant-Volume Bomb: Effects of Operating Variables and Fuel Structure: Proc. API, sec. III, Div. of Ref., vol. 35, 1955, pp. 361-373.

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The principal components of the constant-volume combustion apparatus are shown in figure 12; figure 13 is a cross section of the bomb assembly, and figure 14 shows the bomb, injector, and pressure pickup.

The ignition delays and minimum ignition temperatures of numerous pure hydrocarbons were determined at 250 pounds and 650 p.s.i. at eight temperatures between 500° and 1,390° F. Ignition-delay measurements also were made on two secondary diesel reference fuels.

The authors conclude that the type of combustion that has been studied is extremely complex, and research on many scientific fundamental phases of the problem will be required to develop a detailed understanding of the processes, and that the constant-volume bomb is ideally suited to problems of this type.

Fuel-Heat Gain and Release

The purpose of work done at the Bureau of Mines Petroleum Experiment Station[47] in collaboration with investigators at the University of Wisconsin was to obtain the time history of heat transfer between fuels and air (or other gases) when fuels were injected into a heated and pressurized-bomb-type vessel (constant-volume bomb).

The data show that chemical heat release occurs only after an appreciable interval of time during which the fuel is heated and may be partly or wholly vaporized. The rapidity of this heating--and associated ignition delay--are influenced markedly by the physical properties of the surrounding gas. Fuel volatility and chemical structure have relatively little influence on the rate of heat transfer to the fuel in the prereaction period. It is also shown that the delay period before release of chemical energy and the rate of chemical energy release are influenced both by the chemical composition of the fuels and by gas-to-fuel heat-transfer rates during the prereaction period.

Ignition accelerators were studied to determine how the response of ignition-promoting materials varied with changes in conditions under which autoignition was initiated.[48]

The increased demand for diesel fuel had resulted in the use of increasingly greater percentages of cracked distillates and other low-quality diesel fuels. As these fuels often failed to meet specifications of the cetane number, there was growing interest in the use of ignition-promoting additives to upgrade the fuels. There were also serious questions regarding the true value of the additives. The paper points out that improvement of the cetane number may be determined, but there is doubt that this improvement necessarily

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47/ Hurn, R. W., Chase, J. O., Ellis, C. F., and Hughes, K. J., Fuel-Heat Gain and Release in Bomb Autoignition: SAE Trans., vol. 64, 1956, pp. 703-711 (Society of Automotive Engineers, New York 18, N. Y.

48/ Hurn, R. W., and Hughes, K. J., Ignition Accelerators and Autoignition Environment: Ind. Eng. Chem., vol. 48, No. 10, October 1956, pp. 1904-1908.

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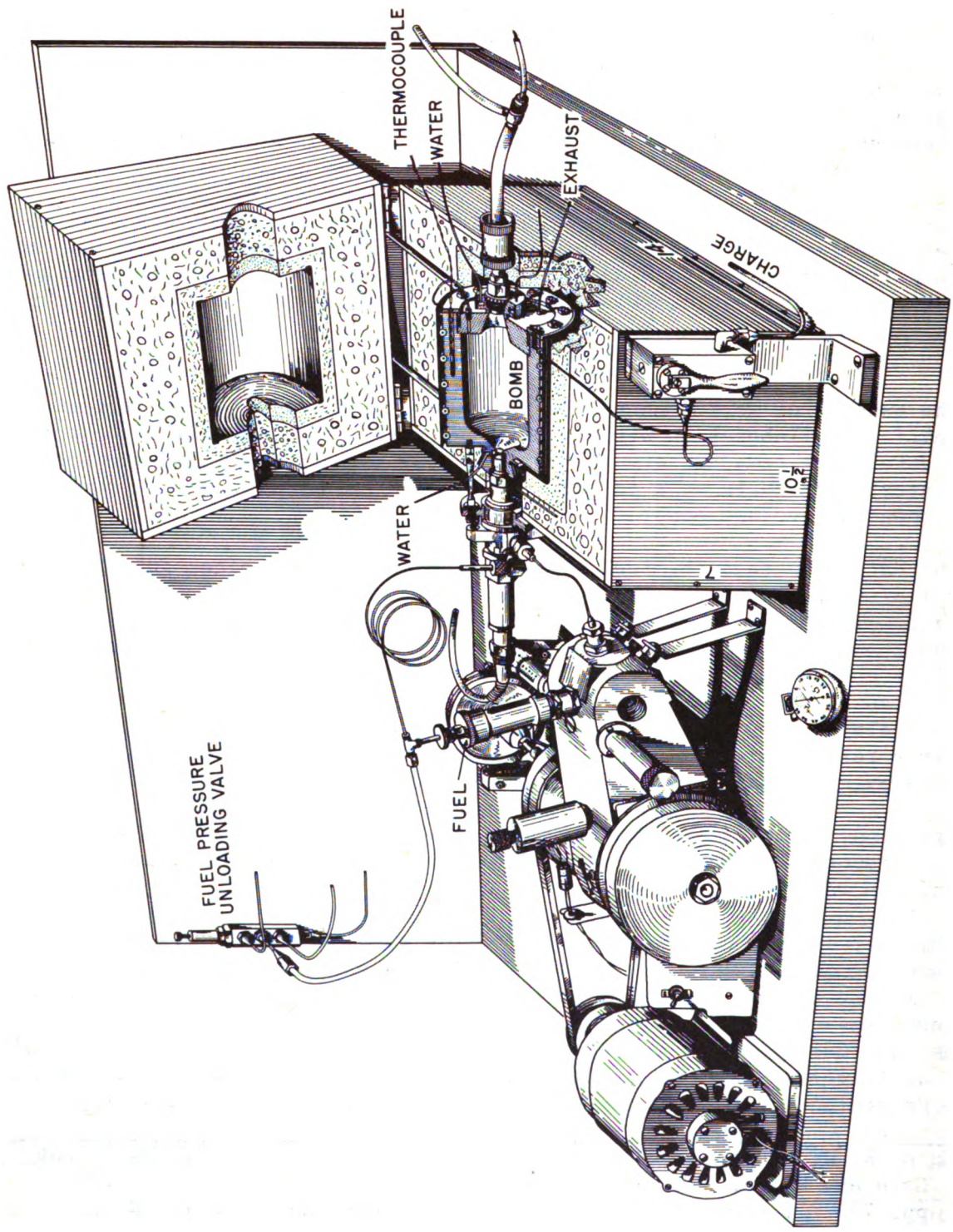

FIGURE 12. - Principal Components of Constant-Volume Combustion Apparatus.

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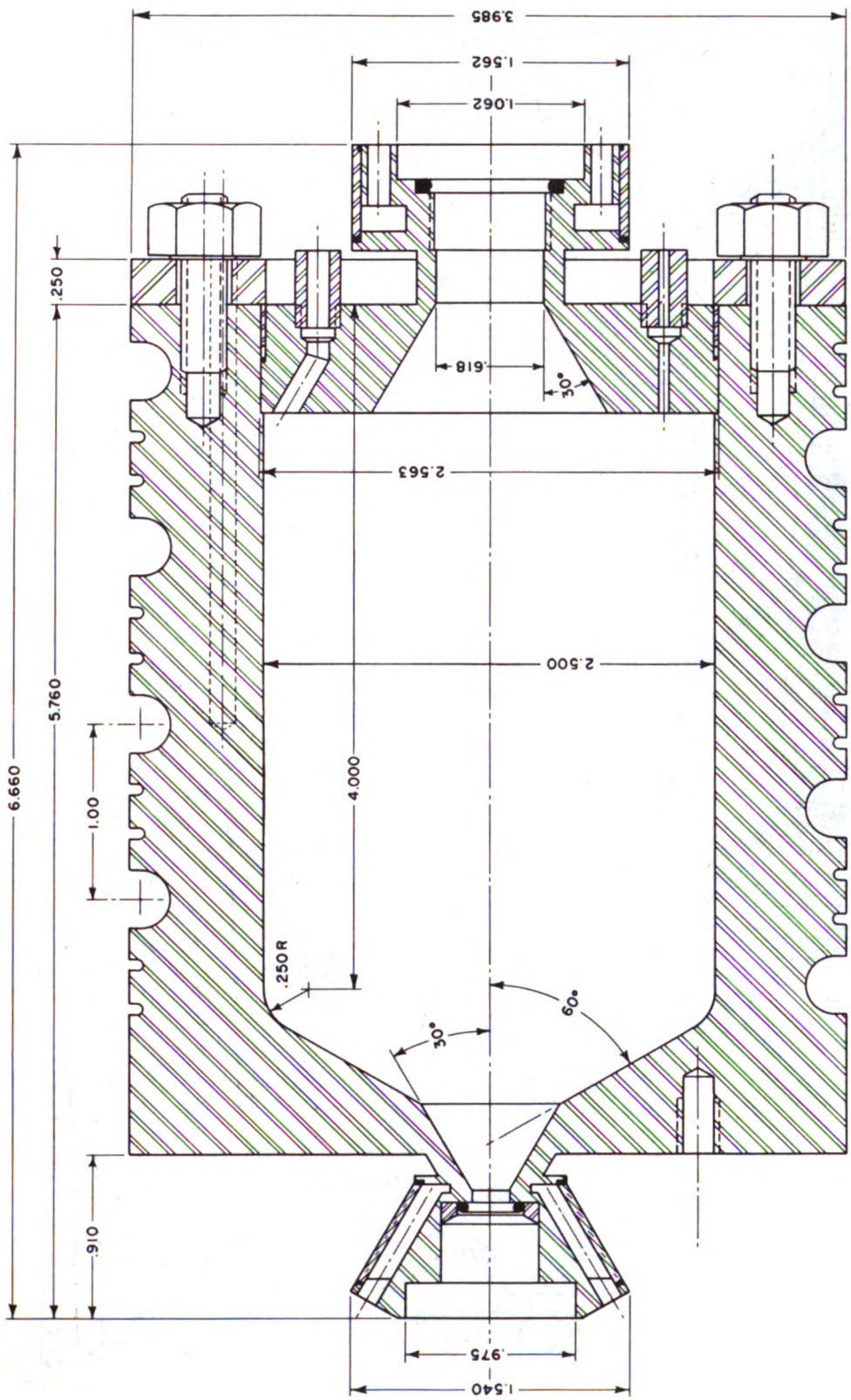

FIGURE 13. - Cross Section of Constant-Volume Combustion-Bomb Assembly With Major Dimensions.

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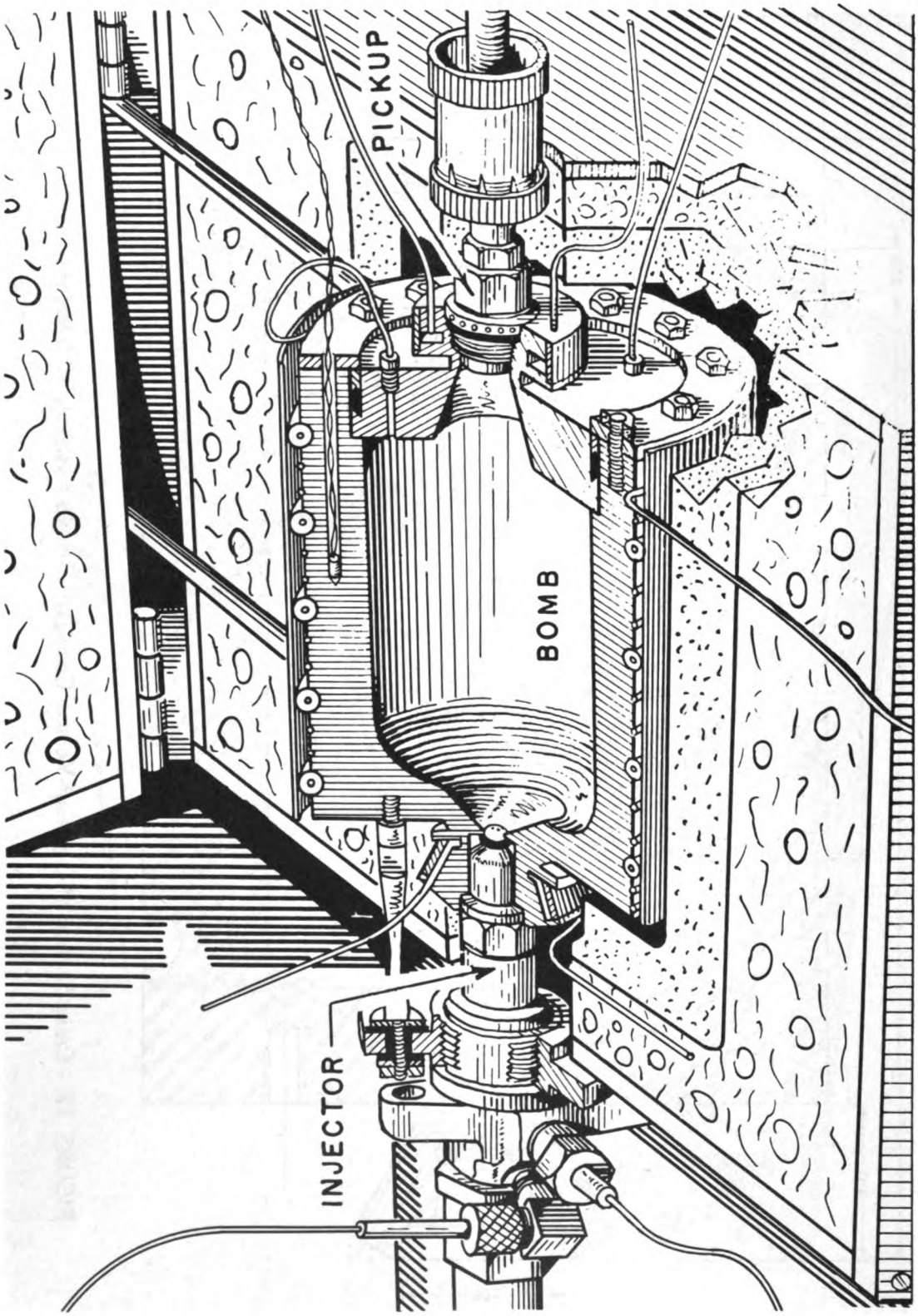

FIGURE 14. - Bomb, Injector, and Pressure Pickup.

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reflects a real proportionate gain in engine performance under conditions of operation that require use of the igntion promoter.

Diesel-Fuel-Specification Requirements

Papers on diesel fuels that were presented at a meeting of Committee D-2 on Petroleum Products and Lubricants of the American Society for Testing Materials in Philadelphia, Pa., February 17, 1954, have been published as a symposium on Diesel Fuels.[49/] A paper on Diesel Fuel Specification Requirements in the symposium by C. C. Ward, chemical engineer at the Bureau of Mines Petroleum Experiment Station, Bartlesville, Okla., points out that the marketed fuels conform fairly well to consumers' specifications, but the ASTM specifications are too broad to enable the consumer to specify the appropriate fuel for his service requirements. The diesel-engine operator with enough volume to dictate his demands will write his own specifications and obtain the fuel he wants because such fuels are available; small operators are left to the dictates of distributors who supply fuels that meet ASTM specifications, but which nevertheless vary widely, depending upon the particular supplier. ASTM has the choice of making its classification (reprinted in the symposium report) realistic and usable, or living with a hundred or more specifications outlined by the individual engine manufacturers and consumers.

Comparisons are drawn in the paper between specifications proposed by 41 engine manufacturers and 28 railroads, with 4 military specifications (as the basis for automotive builders' and consumers' recommendations) and the data of the Bureau of Mines Diesel Fuel Survey 1953[50/] as a measure of properties of fuels marketed.

Precision of Fuel Ratings

The American Society for Testing Materials, through its Committee D-2 on Petroleum Products and Lubricants, has long been associated with the efforts of the petroleum, automotive, and aviation industries in working out standard methods for evaluating the anti-knock quality of various hydrocarbon fuels. In the early thirties the American Petroleum Institute (API) and the Society of Automotive Engineers (SAE), through the jointly sponsored Coordinating Research Council (CRC), set up an arrangement for cooperative studies of fuel ratings with participation of a number of interested laboratories. The Coordinating Research Council was organized in 1922 by the SAE and the API as a means of effecting cooperative effort of these industries in solving problems of mutual interest.

The year 1953 marked the 20th year of monthly cooperative testing of motor gasolines to determine the knock characteristics (octane numbers) of these fuels and to determine the precision of the test methods used. A

49/ American Society for Testing Materials, Symposium on Diesel Fuels: ASTM Special Tech. Pub. 167, Philadelphia 3, Pa., September 1954, 50 pp.

50/ Blade, O. C., National Annual Diesel-Fuel Survey 1953: Bureau of Mines Rept. of Investigations 5008, 1953, 24 pp.

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paper[51] covering the 7-year period 1947 to 1953 represents an analysis of 19,570 engine ratings of 294 fuel samples by the five test methods (motor method, research method, supercharge method, aviation method, and cetane method) as reported by member laboratories and by nonmember participants in the three (motor fuels, aviation fuels, and diesel fuels) semiannual exchange tests.

The reported results indicate a stabilization of precision in rating motor fuels by both the motor and research methods in the last 5 years of the period. The precision for the 7-year period was affected adversely by high "standard deviations" in 1947 and 1948. The research method showed a steady improvement in precision since a high standard deviation in 1944. For the last 5 years of the period the average standard deviation by the motor method is 0.47 octane number, compared with 0.50 for 7 years. Results for the research method showed a 5-year average of 0.36 and a 7-year average of 0.40. The article includes 14 figures (graphs) and 4 extensive tables of data on the samples.

Liquid-Fuel Surveys

During the period of this report the Bureau of Mines continued its surveys of characteristics of marketed motor gasolines, aviation gasolines, diesel fuels, and burner fuel oils.

Motor-Gasoline Surveys

The first Bureau of Mines survey of characteristics of marketed motor gasolines was made in 1915.[52] A second survey was begun about the time the United States entered World War I; its principal purpose was to obtain information regarding the grades and varieties of gasoline on the market so that intelligent and practical specifications could be written for Government purchases. A total of 247 samples was collected from 21 States during the 1917 survey.

A similar and more extensive survey was made by the Bureau of Mines in April to May 1919 to obtain data needed for revision of the Federal motor gasoline specifications. Data on the 1917 and 1919 surveys are presented in Bureau of Mines Bulletin 191.[53]

In January 1920[54] the Bureau of Mines made the first of a series of semiannual surveys of motor gasoline that has continued to the present, except

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51/ Gooding, R. M., and Cleaton, Robetta B., The Precision of Fuel Ratings, 1947 to 1953: ASTM Bull. 293, January 1955, pp. 51-61.

52/ Rittman, W. F., Jacobs, W. A., and Dean, E. W., Physical and Chemical Properties of Gasoline Sold Throughout the Calendar Year 1915: Bureau of Mines Tech. Paper 163, 1916, 45 pp.

53/ Hill, H. H., and Dean, E. W., Quality of Gasoline Marketed in the United States: Bureau of Mines Bull. 191, 1920, 275 pp.

54/ Smith, N. A. C., The Motor-Gasoline Surveys of 1920 and 1921 (a Sequel to Bulletin 191): Bureau of Mines Tech. Paper 328, 1932, 41 pp.

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that no reports were made on motor gasolines sold during the winter of 1941-42 and during the summer of 1942.

The motor-gasoline surveys beginning with the survey for the winter of 1947-48[55] were made in accordance with a cooperative agreement between the American Petroleum Institute and the Bureau of Mines. By agreement with the API, identification of the items in the surveys is confidential.

The gasolines covered by the surveys include those from both large and small suppliers. The data were obtained by laboratories of various refiners, motor manufacturers, and chemical companies and were submitted to the Bureau of Mines for compilation.

The data of each of the semiannual surveys are assembled in five tables and presented graphically in three figures. The tables give average values for gravity, sulfur content, gum content, tetraethyllead content, research and motor octane number, Reid-vapor-pressure and distillation characteristics for different brands (items) in each of 17 districts into which the United States is divided for the purposes of the surveys. Average values for regular-price and premium-price gasolines in each of the 17 districts are tabulated. For the fiscal years 1954-56, inclusive, six reports were issued.[56]

Similar reports are available, free, upon application to the Publications Distribution Section, Bureau of Mines, 4800 Forbes Avenue, Pittsburgh 13, Pa.

Aviation Gasolines and Jet Fuels

Surveys of characteristics of commercial aviation gasolines were begun in 1947 in cooperation with the Coordinating Research Council, Inc. The first report under this agreement was published in May 1948.[57] The report presented data on 71 samples comprising four grades of aviation gasolines submitted by the cooperating companies. Inspection data were furnished by the participating manufacturers, and characteristics of particular interest in the study of vapor-lock problems were determined on the samples in the Bureau of Mines laboratories.

55/ Blade, O. C., National Motor-Gasoline Survey, Winter 1947-48: Bureau of Mines Rept. of Investigations 4354, 1948, 31 pp.

56/ Blade, O. C., National Motor-Gasoline Survey, Summer 1953: Bureau of Mines Rept. of Investigations 5041, 1954, 24 pp. National Motor-Gasoline Survey, Winter 1953-54: Bureau of Mines Rept. of Investigations 5066, 1954, 24 pp. National Motor Gasoline Survey, Summer 1954: Bureau of Mines Rept. of Investigations 5111, 1955, 24 pp. National Motor-Gasoline Survey, Winter 1954-55: Bureau of Mines Rept. of Investigations 5146, 1955, 24 pp. National Motor-Gasoline Survey, Summer 1955: Bureau of Mines Inf. Circ. 7746, 1956, 24 pp. National Motor-Gasoline Survey, Winter 1955-56: Bureau of Mines Inf. Circ. 7763, 1956, 26 pp.

57/ Holliman, W. C., Barker, M. G., and Potts, Nancy, Survey of Commercial Aviation-Gasoline Characteristics, March 1947 Production: Bureau of Mines Rept. of Investigations 4273, 1948, 16 pp.

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Successive reports were published in following years. During the period covered by this account, three reports were issued[58] under a cooperative agreement between the API and the Bureau of Mines. In the reports analytical data are presented for samples of aviation gasoline and of aviation jet fuel. The analyses were made on samples typical of the manufacturers' production in their laboratories, and the results were submitted to the Bureau of Mines for compilation. The analyses of aviation gasolines are tabulated according to the following grades: 80/87, 91/96, 100/130, 108/135, and 115/145. In each grade the analyses are tabulated in the order of commercial only, commercial and military, and military only. Analyses of JP-3, JP-4, and JP-5 jet fuel, and JP-5 referee jet fuel are tabulated in the reports.

National Annual Diesel-Fuel Surveys

In 1950 the Bureau of Mines published the first of a series of annual surveys of diesel fuel characteristics,[59] in cooperation with the API. The report points out that the growing importance of diesel fuel oil has resulted in a need by the petroleum industry, engine manufacturers, and consumers for more information regarding the types and quality of diesel fuels being marketed. To supply this information, the API and the Bureau of Mines conducted a survey of diesel fuel oil produced in refineries in the United States during 1950. Samples of diesel fuel oil representative of actual shipments were analyzed by the manufacturers in accordance with instructions issued by the Fuel Survey Panel of the Automotive Research Committee of the API. Results of the analyses were transmitted to the Bureau of Mines, where the data were studied and compiled by groups in comparable form as shown in the tables of the report. Data on the samples include gravity, flash point, color, viscosity, cloud test, pour point, sulfur content, aniline point, Ramsbottom carbon residue on 10-percent residuum, ash content, cetane number, calculated cetane index, and distillation data. The data are segregated by geographical distribution of the source of the samples.

During the fiscal years 1954-56, inclusive, results of three diesel-fuel surveys were published.[60] The report for 1953 notes that use of diesel fuel had continued to increase to the extent that by April 1953 the monthly production of diesel fuel was 14,300,000 barrels.

58/ Blade, O. C., National Annual Survey of Aviation Gasoline and Aviation Jet Fuel, 1953 Production: Bureau of Mines Rept. of Investigations 5036, 1954, 15 pp. National Annual Survey of Aviation Gasoline and Aviation Jet Fuel, 1954 Production: Bureau of Mines Rept. of Investigations 5132, 1955, 15 pp. National Annual Survey of Aviation Fuels, 1955: Bureau of Mines Inf. Circ. 7747, 1956, 15 pp.

59/ Blade, O. C., National Annual Diesel-Fuel Survey, 1950: Bureau of Mines Rept. of Investigations 4746, 1950, 25 pp.

60/ Blade, O. C., National Annual Diesel-Fuel Survey, 1953: Bureau of Mines Rept. of Investigations 5008, 1953, 24 pp. National Annual Diesel-Fuel Survey, 1954: Bureau of Mines Rept. of Investigations 5084, 1954, 24 pp. National Annual Diesel-Fuel Survey, 1955: Bureau of Mines Inf. Circ. 7737, December 1955, 24 pp.

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Over 300 samples of diesel fuel are represented in the survey for 1955. The fuels were manufactured by 46 petroleum-refining companies in 104 refineries, large and small, throughout the country. The data are divided into four groups according to grade of diesel fuel, and each group is subdivided into five tabulations according to the geographic marketing distribution of the various fuels represented.

National Annual Survey of Burner Fuel Oils

Annual surveys of burner-fuel oils were inaugurated by the Bureau of Mines in 1955 in cooperation with the API.61/ The reports are issued to provide information on the characteristics of the burner-fuel oils currently manufactured for sale. The surveys of burner-fuel oils are similar to the diesel-fuel surveys in pattern and have been conducted under an extension of the same cooperative agreement with the API at the request of the Oil-Heat Institute of America and the petroleum industry. The burner-fuel surveys are not intended to conflict with the diesel-fuel surveys, but rather to supplement them.

Samples of burner-fuel oil typical of their manufacture during the early part of the year under review are analyzed by the refiners in accordance with instructions from the subcommittee on fuel surveys of the Automotive Research Committee of the API. Results of the analyses are transmitted to the Bureau of Mines, where the data are studied and compiled in the tables of the published reports. The data are divided into five groups according to the stated grade of burner-fuel oil, and each group is subdivided into five tabulations according to the geographic marketing distribution of the various fuels. The geographic areas are the same as in the current diesel-fuel surveys.

61/ Blade, O. C., National Survey of Burner-Fuel Oils, 1955: Bureau of Mines Inf. Circ. 7730, 1955, 20 pp. National Survey of Burner-Fuel Oils, 1956: Bureau of Mines Inf. Circ. 7762, 1956, 24 pp.

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